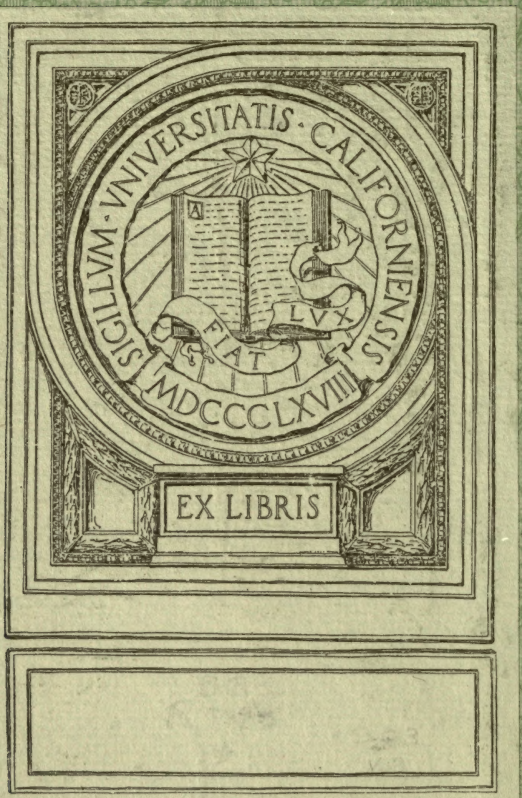
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A TREATISE ON CHEMISTRY

A

TREATISE ON CHEMISTRY

BY

H. E. ROSCOE, F.R.S. AND C. SCHORLEMMER, F.R.S.

VOLUME II.—THE METALS

"*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723

NEW EDITION, COMPLETELY REVISED BY SIR H. E. ROSCOE, ASSISTED BY DRS. H. G. COLMAN AND A. HARDEN

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PREFACE TO VOL. II.

(FIRST EDITION.)

THE aim which the Authors have set before themselves in treating of the Metals and their Compounds is the same as that which they proposed in the discussion of the Non-Metallic Elements. Owing, however, to the large number of the Metals and their Salts, the description of these latter could not, within practicable limits, be made so complete as is possible in the case of the Non-Metallic Compounds. Hence the Authors, whilst giving the characteristic properties of each metal, have been obliged to restrict their notice to those compounds which possess the greatest interest either of a theoretical or practical kind.

Due attention has been paid to the more important technical processes connected with Metallurgy, and no pains have been spared to assist the description of such processes by Drawings of the most modern forms of apparatus and plant.

As an illustration of this the Authors would refer to the Chapter on the Soda and Glass Manufactures in Part I., and to the Metallurgy of Iron in Part II.

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At the end of the volume will be found short Chapters on the Classification of the Elements ; on Spectrum Analysis, so far as the detection of terrestrial matter is concerned.

January, 1878.

PREFACE TO THE THIRD EDITION

During the nineteen years which have elapsed since the publication of the first Edition of this volume of the Treatise, much important work on the chemistry and the Metals and their Compounds has been done. So much indeed that a completely New Edition has been prepared, in which the Metallic Elements and their Compounds have been rearranged and all new matter of importance added. I again have to thank my friends Drs. Colman and Harden for the valuable help which they have given me in this as in the last volume.

H. E. ROSCOE.

September, 1897.

CONTRACTIONS EMPLOYED IN THIS VOLUME

Am. Chem. Journ. = American Chemical Journal.
Amer. J. Sci. = American Journal of Science (Silliman's).
Annalen = Liebig's Annalen der Chemie.
Ann. Chim. Phys. = Annales de Chimie et de Physique.
Ber. = Berichte der Deutschen Chemischen Gesellschaft.
Bull. Soc. Chim. = Bulletin de la Société Chimique de Paris.
Chem. Centr. = Chemisches Centralblatt.
Chem. Zeit. = Chemiker Zeitung.
Compt. Rend. = Comptes Rendues de l'Académie des Sciences.
Gazzetta = Gazzetta Chimica Italiana.
Journ. Chem. Soc. = Journal of the Chemical Society.
J. pr. Chem. = Journal für praktische Chemie.
Journ. Soc. Chem. Ind. = Journal of the Society of Chemical Industry.
Monatsh. = Monatshefte für Chemie.
Phil. Mag. = Philosophical Magazine.
Phil. Trans. = Philosophical Transactions of the Royal Society.
Pogg. Ann. = Annalen der Physik und Chemie (Poggendorf).
Proc. Chem. Soc. = Proceedings of the Chemical Society.
Proc. Roy. Soc. = Proceedings of the Royal Society.
Rec. Trav. Chim. = Recueil des Travaux Chimiques des Pays-Bas.
Wied. Ann. = Annalen der Physik (Wiedemann).
Zeit. anal. Chem. = Zeitschrift für analytische Chemie.
Zeit. angew. Chem. = Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem. = Zeitschrift für anorganische Chemie.
Zeit. phys. Chem. = Zeitschrift für physikalische Chemie.
Zeit. physiol. Chem. = Zeitschrift für physiologische Chemie.

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CHEMISTRY

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CHEMISTRY

THE METALS

1 THE metals gold, silver, copper, iron, tin, and lead were known to the ancients. We find them mentioned in the writings of the Old Testament, as well as in those of the early Greek authors. The name of mercury is first found in the writings of Theophrastus; but the existence of most of the remaining metals only became known in comparatively recent times. Antimony appears to have been obtained in very early times, although the reputed Basil Valentine describes its preparation as a novelty, whilst both zinc and bismuth did not become generally known until the sixteenth century.

An historical notice concerning each metal will be found under its own heading. We have here simply to consider the progress of our knowledge concerning the properties of the metals as a class.

2 The Latin writer who adopted the name of Geber is the first author in whose writings we find a distinct definition of the word metal: "Metallum est corpus miscibile, fusibile, et sub malleo ex omni dimensione extendibile." According to this definition mercury, which had been looked upon as metallic by the Greek alchemists, is not included amongst the metals. Geber likewise distinguished gold and silver as the noble metals, because they do not undergo any change in the furnace, whereas the others were termed base metals. This definition was accepted throughout the whole of the middle ages, so that when the brittle metals antimony, bismuth and zinc came to be well known, they were classed as bastard or semi-metals. Thus for instance, Paracelsus says: "Zinc, which is a metal and yet no metal, and bismuth and the like being partly malleable . . . . are bastards of the

metals;" that is, substances which somewhat resemble them. Opinion was divided respecting the position of mercury, until its solidification by extreme cold and its malleability in this condition had been observed in 1759. From this time forward it was universally admitted to be a metal.

The brilliant experiments and reasoning of Lavoisier towards the close of the eighteenth century finally established the elementary nature of the metals, which hitherto had been looked upon by the followers of Stahl as compounded of a calx united with phlogiston (vol. i., p. 13). In Lavoisier's classification of substances, drawn up in 1787, the metals are grouped together as one of the five classes into which he divided the elements, the distinction between metals and semi-metals being abandoned.

The decomposition of the alkalis by Davy in 1807 made chemists acquainted with substances of an entirely new character. Although the bases of soda and potash agreed "with metals in opacity, lustre, malleability, conductive powers as to heat and electricity, and in their qualities of chemical combination,"[1] and were classed by Davy himself with the metals, yet, inasmuch as they were lighter than water, they were not considered by many chemists to be metals proper. In 1808, Erman and Simon attempted[2] to revive the old distinction between true metals and substances resembling metals by proposing for the new substances the name of metalloids (*μέταλλον* a metal, *εἶδος* similar). This proposal was, however, not generally accepted, and the elements were from this period classed in two groups, the non-metals and the metals, the newly coined term, metalloid, being applied, or rather perhaps misapplied, by Berzelius in 1811 to designate the former of the two classes, in which sense it is still sometimes employed. It soon became evident that the separation of the elements into these two groups was not a logical one, since no satisfactory basis of classification could be obtained. With the discovery of the alkali metals a high specific gravity had ceased to be characteristic, and the property of metallic lustre soon shared its fate. Thus tellurium, discovered in 1782, was grouped with the metals because of its lustre and specific gravity. Its close chemical analogy with sulphur, however, which was pointed out by Berzelius in 1832, clearly indicated that these two elements belong to the same class.

[1] Davy, *Phil. Trans.*, 1808, p. 31. [2] Gilbert's *Annalen*, **28**, 347.

In the same way, every property supposed to be characteristic of a metal has been found to be shared by some one or other non-metallic substance, or to be absent from some otherwise well characterised metal. Thus opacity, and the power of conducting electricity well, were long deemed essential properties of a metal; but we now know that in very thin layers metals such as gold and silver are transparent, whilst several non-metals, such as graphite and selenium, in one of its modifications, conduct electricity like metals.

3 The relations of the so-called non-metals to the metals are well seen when the elements are arranged according to the periodic system (p. 43), which has now superseded the old classification. Thus the elements of the nitrogen group exhibit in a striking manner the gradual transition from a distinctly non-metallic to a distinctly metallic element. Nitrogen itself is undoubtedly a non-metallic body, whilst phosphorus in certain of its allotropic modifications approaches the metals, one of these modifications being, indeed, termed metallic phosphorus. Arsenic, the third member of the nitrogen family of elements, was formerly classed as a semi-metal. At a later period it was considered to be a metal proper, and even now some chemists rank it amongst the metals, whilst others, looking to its striking similarity with phosphorus, place it amongst the non-metals. Antimony and bismuth are elements which belong to this same group, and these substances are always considered to be metals from their close analogy to other distinctly metallic substances. In this case it will be noticed that the members of this group of elements approach more and more closely to a true metal as their atomic weights increase. The same peculiarity is observed in other groups. The elements titanium and zirconium are, on the one hand, closely connected with the non-metal silicon, whilst, on the other, they exhibit the most marked analogies with tin, and are classed accordingly amongst the metals. We must, however, be careful not to draw the conclusion that the elements which possess the highest atomic weights are necessarily metals, and those which possess the lowest are non-metals. Lithium, which next to hydrogen possesses the smallest atomic weight, is a well characterised metal, and hydrogen itself exhibits in its chemical relations far more analogy with the metals than with the non-metals.

Although the division into metals and non-metals is thus seen to be one which does not admit of exact definition, it is

none the less true that the metals as a class do possess certain generic properties which the non-metals either do not possess at all or exhibit only in a very slight degree. Amongst these properties that of metallic lustre may especially be mentioned. This property is characteristic of all metals, and if it is not noticeable when the metals are in the state of fine division, in which case they frequently appear in the form of black powders, it can readily be observed when the powder is rubbed with a hard body.

Another generic difference which may be noticed is that whilst the characteristic oxides of the non-metals belong as a rule to the class of acid-forming oxides, those of the metals are basic oxides, only the higher oxides of certain of the metals being usually capable of forming acids.

DETERMINATION OF THE ATOMIC WEIGHTS OF THE METALS.

4 Although by the year 1819, chemists were in possession of the three principles laid down respectively by Avogadro, Dulong and Petit, and Mitscherlich, by which they are now guided in the selection of the atomic weights of the elements, yet nearly half a century was to elapse before the establishment of a consistent and generally received method of applying these principles.

Avogadro's theory (vol. i., p. 98) proposed in 1811, a few years only after the introduction of the idea of combination between atoms of characteristic weights, rendered necessary a division of the particles even of elementary substances. The chemists of the period were not, however, prepared to admit the validity of these views, and hence they endeavoured to obtain some other foundation upon which to erect a system of atomic weights. Berzelius (1818) found this in the assumption of the identity of volume and atom in the case of the elementary gases, ascribing to water the formula H_2O, and to oxygen the relative atomic weight 16. In deciding upon the atomic weights of the other elements, and especially the metals, Berzelius[1] was forced, like Dalton, to have recourse to purely arbitrary assumptions.

When the important discoveries of Dulong and Petit, and Mitscherlich (vol. i., p. 39) were made, Berzelius at

[1] *Essai sur la théorie des proportions chimiques, etc.*, Paris, 1819.

once saw the simplification which would be effected by the adoption of the theories of these chemists, and in his next table of atomic weights introduced them consistently, thus arriving at atomic numbers, which, with a few exceptions, differ from the modern ones only by small amounts due to the errors of the analytical processes then employed. The chief of these exceptions, potassium, sodium and silver, were due to the great chemical analogy between the strongly basic oxides of these metals and those of calcium, zinc, etc., which led Berzelius, in spite of the known specific heat of silver, to formulate them all on the same type RO, the atomic weights of the three metals mentioned being therefore twice as great as those now employed.

Dumas, on the other hand, at first based his system of atomic weights on Avogadro's theory, but was seduced from his allegiance to this by a false application of it, which had, however, received the countenance of Avogadro himself. Because the molecules of hydrogen, nitrogen, oxygen and chlorine were each supposed according to this theory to be made up of two atoms, Dumas concluded that the same should be true of the molecules of the vapour of any elementary substance whatever. Hence he calculated, on this supposition, the vapour density of sulphur, but found that the experimental density was three times as great as the theoretical. A somewhat similar inconsistency was observed in the case of phosphorus, and Dumas was thus led to abandon Avogadro's theory, whilst Berzelius was induced by the same experiments to modify his theory of the identity of volume and atom in the case of simple substances and to confine it to the simple permanent gases.

The discovery of dimorphism in 1823 had rendered the application of Mitscherlich's theory of isomorphism to the selection of atomic weights somewhat uncertain, so that at this time, about 1830, doubts were cast on the possibility of obtaining any satisfactory method of ascertaining the relative weights of the atoms, and it was proposed that chemists should content themselves with employing the equivalent weights directly determined by analysis.

The equivalent system had been proposed in England by Wollaston[1] at a very early date (1814) and had found very general acceptance amongst his countrymen; it had, moreover, been adopted by Gmelin in his great *Handbook of Chemistry*

[1] A Synoptic Scale of Chemical Equivalents. *Phil. Trans.*, 1814, p. 1.

(1817) and had thus come very generally into use. The tendency to abandon the idea of the chemical atom, as distinct from the equivalent, was moreover strengthened by the fact that Faraday in 1834 found that the electrolytic equivalents of the metals, that is the relative amounts deposited during a given time by a given current of electricity, are identical with their chemical equivalents.

The rapid development of organic chemistry which occurred between the years 1830–1855 made chemists acquainted with many reactions, such as the formation of mixed ethers (Williamson), the acid anhydrides (Gerhardt), the acid ethers, the production of mixed salts of polybasic acids, etc., which could not easily and consistently be formulated on the basis of the equivalent system. Numerous modifications of the system were therefore introduced by individual investigators, until it became quite impossible to interpret a chemical formula without special information as to the sense in which the symbols were employed by the particular author in question.

A most important proposal was put forward by Gerhardt, who, along with Laurent, had resuscitated Avogadro's theory and applied it consistently to all volatile compounds. He regarded all the basic oxides of the metals as derived from water by the replacement of the hydrogen by two atoms of the metal, the general formula of the oxides being R_2O. Silver, potassium and sodium thus received the atomic weights which are now recognised, whilst the atomic weights of metals such as lead, zinc. calcium, etc., had only one-half of the modern values. It will be noticed that in the systems of Berzelius and of Gerhardt, as well as in the equivalent system, the metals silver, potassium and sodium have twice as great an atomic heat as the rest of the metals and therefore form exceptions to the theory of Dulong and Petit.

In 1858, the various conflicting systems were finally co-ordinated by Cannizzaro[1] in his *Sketch of a Course of Theoretical Chemistry*. In this admirable paper, which is one of the classics of chemical literature, he pointed out in detail how a complete and consistent system of formulæ could be obtained by the recognition both of Avogadro's theory and the theory of atomic and molecular heat as founded by Dulong and Petit, and Neumann. The atomic weights suggested by Cannizzaro are the ones we

[1] Sunto di un corso di filosofia chimica fatto nella Reale Università di Genova del Professore S. Cannizzaro. Nuovo Cimento (1858), VII.

still employ, and they were gradually adopted by chemists as soon as they realised the simplicity and consistency of the system. One of the immediate results flowing from the adoption of Cannizzaro's numbers was the periodic system of classification of the elements introduced by De Chancourtois, Newlands, Mendeléeff, and Lothar Meyer.

5 The determination of the atomic weight of an element involves, as has already been pointed out (vol. i., p. 100), two processes. (1) The determination of the proportion by weight in which the element combines with other elements, or, as it is called, the chemical equivalent of the element. (2) The selection of that multiple of the equivalent which represents the smallest amount of the element found in a molecule and is known as its *atomic weight*.

I. Determination of the Equivalent.

6 The equivalent of any two elements is expressed simply by the ratio of the weights of the two which unite to form a compound, or which can replace each other in a compound, but it is usual for the sake of convenience to express all equivalents with respect to some one element, which is chosen as the standard of comparison. In this work, as has already been explained, hydrogen is taken as the standard element. Since only comparatively few of the elements, and especially of the metals, form well-defined compounds with hydrogen, the equivalents to hydrogen have in nearly all cases to be calculated from the numbers experimentally obtained from the compounds of the metal with some other element. The compound of hydrogen which has been analysed with the greatest accuracy is water, and hence, when hydrogen is taken as the standard, nearly all the equivalents involve a knowledge of the equivalent of oxygen to hydrogen. The most accurate determinations of the composition of water show that in it one part of hydrogen is combined with 7·94 parts of oxygen, and hence the latter number represents the equivalent of oxygen. The amount of any other element which combines with or replaces 7·94 parts of oxygen, is therefore taken as the equivalent of that element in the compound in question. Elements which combine in several different proportions have, of course, a corresponding number of different equivalents.

The equivalent weight of an element to oxygen can be most directly determined by the analysis or synthesis of an oxide of the element in question, a process which gives immediately the proportion by weight in which the element combines with oxygen. Thus the equivalents of nickel and iron to oxygen have been determined by reducing a weighed amount of the oxide to the corresponding metal, whilst the inverse process of converting the metal into an oxide has been employed in determining the equivalents of antimony and of bismuth. In most cases, however, this direct process cannot be applied, and recourse is then had to indirect methods of analysis or synthesis. Thus the chlorides of the metals cannot as a rule be directly analysed or synthesised with great quantitative accuracy; it is therefore usually more convenient and accurate to bring a weighed amount of the chloride into reaction with a salt of silver and ascertain either the amount of silver required to combine with the whole of the chlorine present, or the weight of silver chloride produced, or both of these quantities. When this is known, the amount of chlorine present, and therefore the composition of the chloride, can be calculated, provided that the ratio in which silver unites with chlorine, *i.e.* the composition of silver chloride, be known.

Stas found, for example, that 85·031 parts of sodium chloride require 156·862 parts of silver for the complete precipitation of its chlorine in the form of silver chloride. Since 107·13 parts of silver are known to be equivalent to 1 of hydrogen and combine with 35·19 of chlorine to form silver chloride, it follows that the amount of sodium chloride which is required to react with 107·13 parts of silver, and therefore contains 35·19 parts of chlorine, is $\frac{85{\cdot}031 \times 107{\cdot}13}{156{\cdot}862} = 58{\cdot}07$. Hence $58{\cdot}07 - 35{\cdot}19 =$ 22·88 parts of sodium are equivalent to 107·13 parts of silver or 1 part of hydrogen.

In a similar way, the equivalent of an element may be indirectly ascertained by estimating the amount of any substance required for, or produced in, a reaction in which a weighed amount of the element or one of its compounds takes part. The equivalents of a very large number of the metals have accordingly been ascertained by the conversion of an oxide into a salt, or inversely of a salt into an oxide, or of one salt into another. Thus, for example, Erdmann and Marchand found that 100 parts of calcium carbonate yield 136·05 parts of calcium sulphate. From

the known composition and properties of carbonic acid gas and sulphur trioxide, it follows that an increase of weight of 35·79 in this reaction corresponds with 43·67 parts of carbonic acid gas in the original carbonate, and, further, that this is combined with such a quantity of an oxide as contains 15·88 parts of oxygen. Hence 100 parts of calcium carbonate, which gain 36·05 in the reaction, contain $\frac{43{\cdot}67 \times 36{\cdot}05}{35{\cdot}79} = 43{\cdot}99$ parts of carbonic acid gas, combined with 56·01 parts of calcium oxide, and this contains $\frac{15{\cdot}88 \times 36{\cdot}05}{35{\cdot}79} = 16$ parts of oxygen and 40·01 of calcium. Hence, according to this particular experiment, the equivalent of calcium to oxygen is $\frac{40{\cdot}01}{16} = 2{\cdot}5$, whilst the equivalent to hydrogen is $2{\cdot}5 \times 7{\cdot}94 = 19{\cdot}85$. The equivalent of calcium can also be arrived at by means of a similar calculation from the results obtained by the same chemists from the calcination of calc-spar, 13·6031 grams of which were found to yield 7·6175 grams of quicklime on ignition. In other cases the amount of hydrogen which is evolved when a weighed amount of a metal is dissolved in an acid or alkali (aluminium, zinc), the amount of a metal precipitated by a weighed amount of another metal from a solution of one of its salts, the amount of metal deposited by the electrolysis of a weighed amount of a salt (copper), the amount of an acid required to neutralise a weighed amount of a given base, etc., etc., may all be used for the determination of the equivalent, provided that the necessary knowledge of the equivalents of the various other substances involved is available.

In all these indirect processes, in addition to the unavoidable experimental error of the actual estimation, there is also the experimental error involved in each of the equivalents employed in the calculation. The investigator, therefore, in selecting methods for the determination of the equivalent of an element, will, if possible, choose such as involve substances of which the equivalents are known with the greatest accuracy. The experimental error of the actual estimation cannot be entirely removed, but it is diminished by taking the average result of a large number of experiments, and by carefully arranging that the amount of material employed shall be as large as is consistent with the proper execution of the experiment. A further precaution, which should always be taken when it is practicable,

is to determine the equivalent by as many distinct processes as possible, since in this way the special experimental error which is peculiar to each process is to some extent eliminated.

The experimental foundation which is thus seen to be necessary for the construction of a system of equivalents is due in great part to the classical labours of Stas,[1] who carried the processes of analytical chemistry to a degree of accuracy quite unknown to his predecessors, Dalton, Berzelius and Dumas. Stas chose silver as the substance which was most convenient for experimental purposes, and determined its equivalent on the one hand to oxygen, and on the other to the elements chlorine, bromine, iodine, sulphur and potassium, all possible precautions being taken to avoid error. The equivalent of silver to chlorine, bromine and iodine was determined by the direct synthesis of the corresponding compound. In the case of silver chloride, the silver and the silver chloride obtained from it were weighed; "on the other hand the composition of the bromide and iodide was determined by a series of complete synthesis, the metallic silver the bromine or iodine and the silver bromide or iodide being all weighed." The equivalent of silver to oxygen was ascertained by the reduction of silver chlorate, bromate and iodate to the chloride, bromide and iodide. The difference in weight between the oxygenated salt which was taken and the halogen compound which was obtained gives the ratio of oxygen to silver chloride, etc., and the composition of the latter having been ascertained as just described, the ratio of silver to oxygen can be calculated. In another series of experiments designed for the same purpose, potassium chlorate was converted into potassium chloride by heat, and the ratio of potassium chloride to oxygen thus obtained. The amount of silver necessary to combine with the chlorine of a weighed amount of potassium chloride was then determined, and the ratio of silver: potassium chloride: oxygen, thus ascertained. A similar series of experiments was also carried out with the sulphide and sulphate of silver.

In this way, then, the equivalents of silver, chlorine, bromine, iodine, sulphur and potassium to oxygen were all obtained, and these were used by Stas for the determination of the equivalents of sodium, lithium, lead and nitrogen. The probable error in the mean equivalent of silver to oxygen deduced from

[1] Nouvelles recherches sur les lois des proportions chimiques; sur les poids atomiques et leur rapports mutuels. Bruxelles, 1865. 4to.

all these five sets of experiments only amounts to 0·0034 per cent.

The special methods adopted for the determination of the equivalents of the various metals will be found under their several headings.

II. Selection of the Atomic Weight.

7 The methods already described (vol. i., pp. 99–100) for the determination of the atomic weight of an element by ascertaining the molecular weights of a number of its compounds by the vapour density method, and then finding out by comparison the smallest amount of the element which is ever present in a molecule, may be applied without alteration to such of the metals as form volatile compounds. Many of these, however, form such a small number of volatile compounds that the determination of the atomic weight by this method becomes unsatisfactory, and it cannot of course be applied at all to such of the metals as do not form volatile compounds. The molecular weights both of the metals themselves and of their compounds may in certain cases be ascertained by the cryoscopic method of Raoult (vol. i., pp. 111–118).

In cases to which none of these methods can be applied, chemists are guided by the specific heat of the metal and its compounds, its general relations with the other elements, and the isomorphism of its compounds.

Molecular Weights of the Compounds of the Metals.

8 The most readily volatile among the compounds of the metals are the organo-metallic derivatives, which may be looked upon as compounds of the metals with the alcohol radicals. They are usually obtained by the action of a metal on an organic iodide, zinc-methyl being, for example, prepared by the action of zinc on methyl iodide.

$$2Zn + 2CH_3I = ZnI_2 + Zn(CH_3)_2.$$

They are usually liquids which boil at comparatively low temperatures, and their vapour density can therefore be determined by the ordinary methods, except that, as they are very

readily oxidised in the air and are usually spontaneously inflammable, the determinations must be carried out in an atmosphere of an indifferent gas, such as nitrogen. In addition to these compounds of the metals with the alcohol radicals, the remarkable compounds of nickel and iron with carbonic oxide serve for the same purpose. Volatile organic compounds of which the vapour density has been determined are formed by the following metals ; Zn, Hg, Al, Sn, Pb, Sb, Bi, Ge, Fe, and Ni.

In addition to the organo-metallic derivatives, many metals form compounds with the halogen elements volatilising at moderate temperatures, and of which the vapour density can therefore be determined. In a few cases the vapour density of the metal itself has been found to be of value in deciding upon the atomic weight.

The experimental methods of ascertaining the vapour density of substances which are only volatile at high temperatures differ somewhat from those ordinarily employed. The older determinations of Deville and Troost, Roscoe and others were carried out by Dumas' method, a bulb of porcelain, which can be sealed by means of the oxy-hydrogen jet, being used for temperatures above that at which glass softens. The great difficulty inherent in this process is the determination of the temperature, which must be known with considerable accuracy. This was either determined calorimetrically, by the aid of a weighed mass of platinum, or by the use of a second similar bulb containing iodine or mercury, the temperature being calculated from the amount of vapour left in this second bulb under the conditions of the experiment. This process has now been superseded by that of Victor Meyer, which was originally introduced for this purpose, and presents the great advantage that a knowledge of the temperature of the experiment is not involved in the calculation of the results. An apparatus constructed of, or lined with, porcelain or platinum is employed and is heated to the requisite temperature either by the vapour of some substance of high boiling point, or by a gas or wind furnace. It is of course essential that the temperature of the apparatus be maintained constant throughout the duration of the experiment. The air in the apparatus is usually displaced by nitrogen, to prevent the oxidation which would otherwise occur in many cases at the high temperature employed. The interpretation of the experimental results is often rendered difficult by the complete or partial dissociation of the com-

pound, either into two similar or two dissimilar molecules, which is rendered evident by the fact that the relative vapour density varies with the temperature at which it is determined. Several cases of this kind are discussed under the heading of valency (p. 33).

Atomic Heat.

9 The specific heat of a body is the ratio of the quantity of heat required to raise the temperature of that body 1° to the quantity required to raise that of an equal weight of water 1° (Maxwell). The amount of heat needed to raise a kilogram of water through 100° is thirty-one times as large as that required to raise the same weight of platinum through the same interval of temperature, or in other words, the same amount of heat which raises one kilogram of water through 100° will raise thirty-one kilograms of platinum through the same temperature; hence the specific heat of platinum is said to be $\frac{1}{31} = 0{\cdot}032$. The specific heat of the same substance varies considerably under different physical conditions and according as the substance is solid, liquid, or gaseous.

A careful determination of the specific heat of thirteen of the solid elements by Dulong and Petit in the year 1819,[1] showed that a simple relation exists between the chemical equivalent and the specific heat of these substances. When the numbers representing these two quantities were multiplied together in the case of each of the elements in question, the products were found either to be equal or to stand in a very simple ratio. By a supposition analogous to that made by Avogadro with respect to the combination of gases by volume, Dulong and Petit concluded that the specific heat of the metals varies inversely as the atomic weight, and proposed to adopt as the relative atomic weights of the metals those numbers which, multiplied by the specific heat, gave a constant product. Having thus modified the atomic weights which were at that time received, the French experimentalists proposed the theory that *the atoms of different elements possess the same capacity for heat*, or *all the elements have the same atomic heat*. Although chemists at the time acknowledged the importance of this theory, they did not consider that the conclusions arrived at were established beyond doubt, inasmuch as the alterations in

[1] *Ann. Chim. Phys.* **10**, 395.

the atomic weights introduced by Dulong and Petit, although admissible in some cases, led in other respects to very improbable conclusions. Moreover, a few of the elements investigated by the French chemists were very impure, so that the specific heats which they obtained were inexact. Berzelius very properly insisted that further investigation was necessary, and adds,[1] "If we attempt to apply this idea to compound bodies, and if the result of such an examination confirms the views of Dulong and Petit, this discovery will rank as one of the most important parts of theoretical chemistry."

The next step in the direction thus indicated by Berzelius was made by F. Neumann,[2] who showed in the year 1831 that equivalent quantities of similarly constituted compounds possess equal specific heats, and that this equality is independent of difference in crystalline form; thus calc-spar and arragonite both possess the same specific heat. Neumann, however, did not connect this discovery of the relation between the specific heats of the compounds with that of Dulong and Petit respecting the specific heats of the elements. Only by degrees, and in the hands of numerous observers, was this connection brought about, and even at the present day it cannot be said that the subject is fully investigated. The researches which have mainly contributed to the development of this subject are those of Hermann, 1834, Regnault, 1840, De La Rive and Marcet, 1840, Joule, 1844, Woestyn, 1845, Garnier, 1852, Cannizzaro, 1858, H. Kopp, 1864[3] (whose memoir contains a historical introduction to the whole subject).

It is especially to the researches of Regnault that we are indebted for the corroboration of the results of the earlier experiments proving that the theory of Dulong and Petit is applicable with a very considerable degree of accuracy to about forty of the elementary bodies, so that we may regard those weights of the elements to be their atomic weights, which, when multiplied into the specific heats of the elements, give a constant number. This is termed the capacity of the atom for heat, or the atomic heat of the element. If the atomic weight of hydrogen be taken as the unit, and if the capacity of water for heat be taken as one, then the numbers representing the atomic heats of most of the elements are found to lie near 6·3, or these elements possess the same atomic heat. This is clearly seen if

[1] Berzelius's *Jahresb.* **1**, 19.
[2] *Pogg, Ann.* **23**, 1.
[3] *Annalen*, 1864, Suppl. **3**, 1.

we multiply the specific heats of the metals by their corresponding atomic weights, for example :—

	Specific heat.		Atomic weight.		Atomic heat.
Lead . . .	0·0315	×	205·4	=	6·5
Platinum .	0 0324	×	193·3	=	6·3
Silver . . .	0·0570	×	107·13	=	6·1
Tin	0·0548	×	117·2	=	6·4
Zinc . . .	0·0955	×	65·0	=	6·2

The researches of Regnault and Kopp have proved that Dulong and Petit's theory is approximately true for the greater number of the elements in the solid state and within a given range of temperature, so that this property may be employed for the purpose of controlling the determinations of atomic weight in doubtful cases. Amongst those elements which conform to the theory are in the first place the metals, and then certain non-metals such as bromine, iodine, selenium, tellurium, and arsenic.

The following table shows within what limits the atomic heat of the different elements varies. The first column contains the names of the elements, the second their specific heats, the third the mean temperature at which the determination was made, the fourth the atomic weight, the fifth the product of the atomic weight into the specific heat, and the sixth the name of the observer :—

I.	II.	III.	IV.	V.	VI.
Lithium . .	0·9410	+64°	6·98	6·6	Regnault.
Sodium . .	0·2930	−14	22·87	6·7	„
Magnesium .	0·2500	+60	24·2	6·0	„
Aluminium .	0·2140	+60	26·9	5·8	Hillebrand.
Potassium .	0·1660	−34	38·85	6·4	Regnault.
Calcium . .	0·1700	+50	39·7	6·7	Bunsen.
Titanium . .	0·1125	+50	47·7	5·4	Nilson and Pettersson.
Chromium .	0·1216	+50	51·7	6·3	Jäger and Krüss.
Manganese .	0·1220	+55	54·6	6·7	Regnault.
Iron . . .	0·1140	+58	55·6	6·3	„
Cobalt . . .	0·1070	+55	59·4	6·3	„
Nickel . . .	0·1080	+55	58·6	6·3	„
Copper . .	0·0952	+58	62·8	6·0	„
Zinc . . .	0·0955	+55	65·0	6·2	„
Gallium . .	0·0790	+18	69·4	5·5	Berthelot.
Germanium .	0·0757	+220	71·8	5·4	Nilson and Pettersson.
Arsenic . .	0·0822	+56	74·4	6·1	Neumann.
Selenium . .	0·0840	+42	78·5	6·6	Bettendorf & Wüllner.
Bromine . .	0·0843	−51	79·36	6·7	Regnault.
Molybdenum.	0·0722	—	95·2	6·9	„
Rhodium . .	0·0580	+55	102·0	5·9	„
Ruthenium .	0·0611	+50	103·0	6·3	Bunsen.
Palladium .	0·0593	+55	104·7	6·2	Regnault.
Silver . . .	0·0570	+55	107·13	6·1	„
Cadmium. .	0·0567	+55	111·3	6·3	„
Indium . .	0·0570	+50	112·8	6·4	Bunsen.
Tin	0·0548	+34	117·2	6·4	Kopp.
Antimony .	0·0523	+31	119·4	6·2	„
Tellurium. .	0·0475	+36	124·0	5·9	„
Iodine . . .	0·0541	+59	125·91	6·8	Regnault.
Barium . .	0·0500	—	135·97	6·8	Mendeléeff.
Lanthanum .	0·0448	+40	137·5	6·2	Hillebrand.
Cerium . .	0·0448	+40	139·0	6·2	„
Tungsten . .	0·0334	+55	182·6	6·1	Regnault.
Osmium . .	0·0311	+60	189·3	5·9	„
Iridium . .	0·0326	+60	191·7	6·2	„
Platinum . .	0·0324	+55	193·3	6·3	„
Gold . . .	0·0324	+55	195·7	6·3	„
Mercury . .	0·0319	−59	198·9	6·3	„
Thallium . .	0·0335	+58	202·6	6·8	„
Lead . . .	0·0315	+34	205·4	6·5	Kopp.
Bismuth . .	0·0305	+34	206·4	6·3	„
Uranium . .	0·0276	—	237·6	6·6	Zimmermann.

10 In the foregoing table the following elements, which have been found to possess smaller atomic heats, have been omitted :—

I.	II.	III.	IV.	V.	VI.
Beryllium .	0·4079	—	8·99	3·7	Nilson & Pettersson.
Boron . .	0·244	+55°	10·74	2·6	Regnault.
Diamond .	0·147	+45	11·91	1·8	„
Graphite .	0·198	+50	11·91	2·4	„
Gas Carbon .	0·185	+36	11·91	2·2	„
Sulphur . .	0·163	+31	31·82	5·2	Kopp.
Silicon . .	0·173	+55	28·2	4·9	Regnault.
Phosphorus .	0·174	−34	30·8	5·4	„

These elements accordingly possess at temperatures between 0° and 100°, smaller atomic heats than correspond to Dulong and Petit's theory. Weber's[1] investigations have shown that the specific heat of carbon varies very considerably with the temperature, and that above a certain limit of temperature it remains constant and then agrees with Dulong and Petit's theory, as is seen in the following table :—

	Specific Heat.			Atomic Heat.
Diamond	0·0635	−	50·5°	0·76
„	0·1128	+	10·7	1·34
„	0·1532		58·3	1·83
„	0·2218		140·0	2·64
„	0·2733		206·1	3·26
„	0·4408		606·7	5·25
„	0·4489		806·5	5·35
„	0·4589		985·0	5·47
Graphite	0·1138	−	50·3	1·36
„	0·1990	+	61·3	2·37
„	0·4454		641·9	5·31
„	0·4670		977·9	5·56

Similar results have been obtained in the case of silicon. The specific heat of this element increases from 0·1360 at

[1] *On the Specific Heat of the Elements Carbon, Boron, and Silicon.* Stuttgart, 1874.

−39·8° to 0·2029 at 232°, above which it appears to remain constant, the atomic heat then being 5·7. Boron also exhibits the same phenomenon, the specific heat increasing from 0·1965 at −39·6° to 0·3663 at 233° and probably becoming constant at about 500–600°.

The same investigator has also shown that the allotropic modifications of a substance at low temperatures possess different specific heats, but that this difference diminishes as the temperature increases, and at last altogether disappears. For example, Regnault concluded from his experiments that the specific heat of amorphous carbon was different from that of the two other modifications. Weber has, however, distinctly shown that this is not the case, but that carbon exists in two thermal modifications, (1) opaque, (2) transparent. These thermal differences only occur at low temperatures, and when a high temperature is reached no variation is observed.

From the table we see that the atomic heats of the elements differ from one another considerably even within the limits of temperature at which each appears to be constant. Thus, for instance, whilst the value for the majority lies between 6·1 and 6·6, in others the number sinks so low as 5·4, and in the case of the alkali metals and bromine and iodine the number rises to as much as 6·8. These differences may, in some instances, be explained by the fact that the substances under investigation were impure. They may also be due, to a certain extent, to errors of experiment which may easily occur in working with bodies so readily oxidised as the metals of the alkalis. It must also be remembered that the specific heat of most substances varies with the temperature, although not usually to so great an extent as in the case of carbon, silicon, &c., considered above. Thus the specific heat of silver increases between 0° and 500° by 15·5 per cent. of its whole value, whilst in the case of iron the increase between the same limits is no less than 60 per cent. Since this is the case, and the specific heats of the different elements vary in a different manner with the temperature, it will be seen that the agreement between the atomic heats can only be a general one.

We must also bear in mind that when we speak of specific heat, we really refer to a complex quantity, which comprises not only the heat which actually goes to raise the temperature of the heated body, but also that which is expended in performing work, such as expansion or diminution of the cohesion of the

particular body. This last amount of heat is different for different substances, whilst the first amount is theoretically the same for a molecule of any substance.

The above theory does not apply to liquid or gaseous bodies with the single exception of mercury, which possesses the same atomic heat in the liquid and in the solid state.

The most important evidence in favour of the validity of the hypothesis of Dulong and Petit is the fact that the results deduced from it agree with those deduced from Avogadro's theory for those metals which form volatile compounds, and with which, therefore, such a comparison can be instituted.

Molecular Heat of Compounds.

11 The law that the molecular heat of a compound is equal to the sum of the atomic heats of its elements, or that the atomic heat of an element does not undergo change when that element enters into combination, was first laid down by Joule,[1] but its experimental verification is chiefly due to Kopp. The following examples will illustrate this:—

		Specific Heat.	Molecular Heat. Found.	Molecular Heat. Calculated.
Potassium bromide	KBr	0·1070	12·7	13·1
Mercuric iodide . .	HgI_2	0·0423	19·1	19·9
Lead iodide . . .	PbI_2	0·0427	19·5	20·1
Lead bromide . .	$PbBr_2$	0·0533	19·4	19·9

Hence if the atomic heat of a solid element has not been determined it may be calculated from the molecular heat of its compounds with other elements whose atomic heat is known. In this way the atomic heats of rubidium, strontium, barium, and titanium have at various times been determined, and they have been found to agree with the theory which comprises all the other metals.

Kopp has also shown that the elements which are unknown in the solid state possess a constant atomic heat in their solid compounds. It thus becomes possible to determine the amount of their atomic heat. In this way the atomic heat of chlorine has been found to be equal to 5·9, that of nitrogen 5·3, of fluorine

[1] *Phil. Mag.* 1844 [3], **25**, 334.

5·0, of oxygen 4·0, and of hydrogen 2·3. The following examples illustrate this point:—

		Specific Heat.	Molecular Heat. Found.	Molecular Heat. Calculated.
Silver chloride . .	$AgCl$	0·089	12·7	12.0
Zinc chloride. . .	$ZnCl_2$	0·136	18·5	18·0
Potassium platinochloride. . . .	K_2PtCl_6	0·118	56·9	54·5
Ice	H_2O	0·478	8·5	8·6
Mercuric oxide . .	HgO	0·048	10·3	10·3
Calcium carbonate.	$CaCO_3$	0·206	20·4	20·6
Potassium sulphate	K_2SO_4	0·196	33·9	34·0
Hexachlorethane .	C_2Cl_6	0·177	41·6	39·2

These numbers show that the first two elements agree with the theory. Fluorine does so approximately, but oxygen and hydrogen are seen to deviate considerably.

Kopp has moreover proved that the elements boron, silicon, and carbon possess, in combination, the same atomic heat as in the free state at temperatures below 100°. Hence it is not improbable that if we could obtain the specific heat of oxygen and hydrogen compounds at a high temperature the atomic heats of these elements might exhibit the same sort of alteration which has been proved to occur in the case of carbon, silicon, and boron.

The elements which possess a smaller atomic heat than the majority at temperatures below 100° have low atomic weights and with the exception of beryllium are non-metals (p. 18). All the non-metals whose atomic weights are high and the remaining metals agree with Dulong and Petit's theory below 100°.

12 As instances of the employment of the atomic heat for determining the atomic weight the following may be quoted.

Thallium shows many analogies on the one hand with the alkali metals and on the other with lead, and it was for some time a matter of doubt whether the chloride should be formulated as $TlCl_2$, in which case the atomic weight would be 405·2 or as $TlCl$, the atomic weight being then 202·6. Regnault determined the specific heat of thallium to be 0·0335 and thus decided the question in favour of the latter view, since $0{\cdot}0335 \times 202{\cdot}6 = 6{\cdot}8$.

A similar instance occurs in the case of indium, the chloride

of which contains 37·6 parts by weight of metal to 35·19 parts by weight of chlorine. Indium, however, exhibits a very considerable resemblance to zinc and cadmium, and for this reason the chloride was supposed to have the formula $InCl_2$, giving an atomic weight of 75·2 to the metal. In 1870 Bunsen[1] ascertained by means of his ice calorimeter that the specific heat of indium is 0·057. Now $0·057 \times 75·2 = 4·3$, or only two-thirds of the atomic heat of the other metals. Hence we must assume that the true atomic weight of the metal is $75·2 \times \frac{3}{2} = 112·8$. This gives the formula for the chloride, $InCl_3$, and this has been confirmed by the vapour density.

The example of uranium may also be quoted. At one time this metal was supposed to have an atomic weight of about 119 and to resemble iron in its chemical characteristics, its oxides being assigned the formulæ UO and U_2O_3. At a later period, however, it was found that the chemical relations of the metal agreed better with the atomic weight 237·6 according to which its oxides are UO_2 and UO_3. This conclusion was confirmed by Zimmermann who found its specific heat to be 0·0276 and, therefore, its atomic weight to be about 238.[2]

Isomorphism.

13 An account has already been given of the general phenomena of isomorphism (vol. i., p. 865). As briefly mentioned in the historical introduction (vol. i., p. 39), Mitscherlich was the first to perceive that substances which are similar in crystalline form are also similar in chemical composition; he concluded from his observations that the same number of atoms combined in the same way produces the same crystalline form, this latter being independent of the chemical nature of the atoms and depending only on their number and relative position. He soon afterwards pointed out that this relation might be employed for the determination of the relative combining weights of two elements or compounds. Thus, having found that potassium sulphate and potassium selenate, which crystallise in the rhombic system, are isomorphous, he concluded that selenic acid (the anhydride) would, like sulphuric acid, contain three times as much oxygen as the base with which it was combined

[1] *Phil. Mag.* 1871 [4], **41**, 161, 392.
[2] *Annalen*, 1885, **232**, 299.

in the salt in question, this conclusion being afterwards confirmed by analysis.

At the time when Mitscherlich first stated his theory of the relation between atomic composition and crystalline form, the only available means of ascertaining the atomic weights of the metals was that provided by Dulong and Petit's theory of atomic heat, which had only been applied to some thirteen elements. The theory, moreover, had not at that time been extended to the molecular heat of compounds, and hence the atomic weights of a large number of metals could only be determined by analogy or by arbitrary assumptions. Under these circumstances, Mitscherlich's theory of isomorphism proved of great importance and was at once applied by Berzelius to the determination of the atomic ratios of such elements as chromium, titanium, etc. Thus the ratio of the amounts of oxygen in chromium sesquioxide and chromic anhydride per unit of chromium was known to be 1 : 2, the simplest expression of which, according to the Daltonian system, would be by the formulæ, CrO and CrO_2. Chromium sesquioxide, however, is isomorphous with ferric oxide, iron being an element of which the atomic weight had been determined by the specific heat method, and hence the formula Cr_2O_3 was given to it. Chromic anhydride thus became CrO_3, which is in full agreement with the fact that the chromates are isomorphous with the sulphates, sulphuric anhydride having been formulated by Berzelius on independent grounds as SO_3.

At present the isomorphous relations of the compounds of an element only supply additional confirmation of the atomic weight, which has now been determined for every element either from the molecular weight of its compounds, from the atomic heat of the element itself, or from the molecular heat of its compounds. It was at first thought that identity or very close resemblance of the crystalline forms of two substances was sufficient to stamp them as isomorphous. It has, however, been been found that substances often crystallise in very similar forms, although they have no similarity in chemical composition. Substances are therefore not considered as isomorphous unless they are capable of crystallising together in mixed crystals in which the two substances occur in relative proportions which may be *gradually* varied. Such crystals are characterised by the fact that their physical properties, such as specific gravity, index of refraction, etc., are strictly the mean of the corresponding

properties of their constituents. Sodium nitrate, for example was formerly supposed to be isomorphous with calcite, because the two have nearly the same crystallographic constants, and pieces of calcite when suspended in a saturated solution of sodium nitrate, which is allowed to evaporate, become uniformly covered with sodium nitrate, just as would a crystal of the latter salt itself. In the absence of mixed crystals of these two substances, however, they are no longer looked upon as isomorphous. In the same way all substances which crystallise in the regular system have the same crystallographic constants, but are not looked upon as isomorphous unless, like the alums, they are capable of forming mixed crystals.

Substances which are truly isomorphous, as just defined, are found in all cases to have analogous chemical composition and this may, therefore, be taken as a confirmation of the atomic weights in use, on which the analogous formulæ depend.

The elements may be grouped into the following series,[1] the members of which form isomorphous compounds. Elements which form several series of compounds are often found in a corresponding number of isomorphous series, the isomorphous relations of one type of compound being different from those of another.

(1) (*a*) K, Rb, Cs, Tl, (NH_4).
(*b*) Li, Na, Ag.
(2) (*a*) Be, Mg, Zn, Cd, Mn, Fe, Co, Ni, Os, Ru, Pd, Pt, Cu.
(*b*) Ca, Sr, Ba, Pb.
(3) La, Di, Y, Ce, Er.
(4) Al, Fe, Cr, Co, Mn, Ir, Rh, Ga, In, (Ti).
(5) Cu, Hg, Pb, Ag, Au.
(6) Si, Ti, Ge, Zr, Sn, Pb, Th, Mo, Mn, U, Ru, Rh, Ir, Os, Pd, Pt, Fe.
(7) N, P, As, V, Sb, Bi.
(8) Nb, Ta.
(9) S, Se, Cr, Mn, Mo, W, As, Sb, Fe, Te (?).
(10) F, Cl, Br, I, Mn, (CN).

No cases of isomorphism have as yet been observed among the compounds of the following elements.

H, B, Sc, Yt, C, O, and Tr.

[1] Arzruni, *Physikalische Chemie der Krystalle.* Vieweg, 1895. Sonder-Abdruck aus Graham-Otto's *Ausführlichem Lehrbuch der Chemie*, 1 Band. 3 Abtheilung.

The details of the isomorphous compounds of the metals included in the above series will be found under the several metals.

The Molecular Weights of the Metals.

14 The metals as a rule boil at exceedingly high temperatures, and up to the present it has for this reason only been found possible to obtain definite results with the vapour densities of zinc, cadmium and mercury, all of which form monatomic molecules.[1] On the other hand, the densities of antimony and bismuth, at temperatures of 1,600–1,700° are greater than those required for a monatomic molecule, but less than the numbers corresponding with a diatomic molecule, and a similar uncertainty exists with regard to thallium. The vapour densities of potassium and sodium have only been approximately determined, since the vapours of these metals attack the material of which the apparatus is constructed. The results however point to the conclusion that these two metals form monatomic molecules.

The molecular weights of many of the metals have also been determined by the cryoscopic and vapour-pressure methods of Raoult (vol. i., pp. 114–5). The general result of these experiments is to render it probable that in nearly all cases the molecules of the metals are identical with their atoms. When tin is used as a solvent for the metals Ni, Ag, Au, Cu, Tl, Na, Pd, Mg, Pb, Zn, Cd, Hg, Bi and Ca, the solutions which are formed are found to behave on cooling in the same manner as dilute solutions of nonelectrolytes in water (*loc. cit.*). Atomic proportions of these metals when added to a fixed amount of tin, so as to produce a dilute solution of the metal, all produce the same depression of its freezing point, and the amount of this depression agrees with that calculated from theoretical considerations on the assumption that the molecular weights of these metals are identical with their atomic weights. The numbers obtained for indium and aluminium seem, however, to indicate that the molecules of these metals contain two atoms.[2] The freezing-points and vapour-pressures of solutions of the metals in mercury have

[1] Biltz and Meyer, *Zeit. Phys. Chem.* 1889, **4**, 264; Biltz, *Zeit. Phys. Chem.* 1896, **19**, 385.

[2] Heycock and Neville, *Journ. Chem. Soc.* 1890, i. 376.

also been examined and lead to similar conclusions, although the results obtained are not so regular as when tin is used as the solvent.[1]

15 The identity of atom and molecule has been confirmed in the case of mercury by means of a physical method which is of great importance, as it appears to provide an independent mode of ascertaining whether the molecule of an element contains one or more atoms, without any reference to the compounds of the element. When a gas is heated, the amount of heat required to raise its temperature by a given amount (its specific heat) depends on the conditions under which the gas is maintained. If the gas be allowed to expand, its specific heat is found to be greater than when it is heated at constant volume. The difference between the two specific heats represents the amount of heat equivalent to the work which is done by the gas in expanding against the atmospheric pressure and can readily be calculated. This being known, the specific heat at constant volume, can be obtained by subtracting it from the specific heat at constant pressure, and the result thus obtained agrees with that obtained by direct experiment.

For an ideal monatomic gas not only can the specific heat under constant volume be calculated from that observed under constant pressure as just described, but in addition to this both the specific heat at constant volume, and that at constant pressure can be calculated directly according to the kinetic theory of gases. The result of this calculation is that the ratio of these two (k) is 1·66. The ratio actually found for the elementary gases oxygen, hydrogen, nitrogen, and other gases which contain two atoms in the molecule is, however, about 1·4. The explanation of this discrepancy is that when two atoms are present in the molecule, a portion of the heat is spent in producing relative motion between these two atoms, this being summed up as internal work. The heat taken up by such a gas as oxygen therefore may be considered as made up of three different parts. H_t, that required to actually increase the mean kinetic energy of the molecule, which is the same for all gases; H_e, that equivalent to the work done by the gas expanding against external pressure, which is nearly the same for all gases; H_i, the amount equivalent to the internal work done in the molecule

[1] Tammann, *Zeit. Phys. Chem.* 1889, **3**, 441; Ramsay, *Journ. Chem. Soc.* 1889, i. 521.

of the gas, which is different in different gases. The ratio between the two specific heats of a gas like oxygen may therefore be expressed by the fraction $\frac{H_t + H_e + H_i}{H_t + H_i}$ which is always less than $\frac{H_t + H_e}{H_t}$ the expression for a monatomic gas.

The ratio between the two specific heats can be experimentally ascertained by measuring the velocity of sound in the gas in question and then applying the equation $u = \sqrt{kg\frac{p}{d}}$ (where u = the velocity of sound in the gas, p the pressure, d the density, g the intensity of gravity, and k the ratio of the two specific heats), which holds for sound waves in gaseous media. The result of such an experiment with mercury vapour carried out by Kundt and Warburg [1] gave the value 1·66 for the ratio of the two specific heats.

These investigators thereupon pointed out that this shows that no internal work is done when mercury vapour is heated, the most probable explanation being that the molecule of mercury does not contain two atoms but only one. This supposition, as we have seen, is quite in agreement with the observed vapour density of mercury.

The two gases, argon and helium, behave in a similar manner to mercury vapour, the ratio of specific heats determined by the above method being 1·659 and 1·652 respectively.[2] No independent means of ascertaining the atomic weights of these two gases is at present available (1896), and it is impossible to say whether the absence of internal work is actually due to the identity of atom with molecule, as in the case of mercury, or to some other cause.

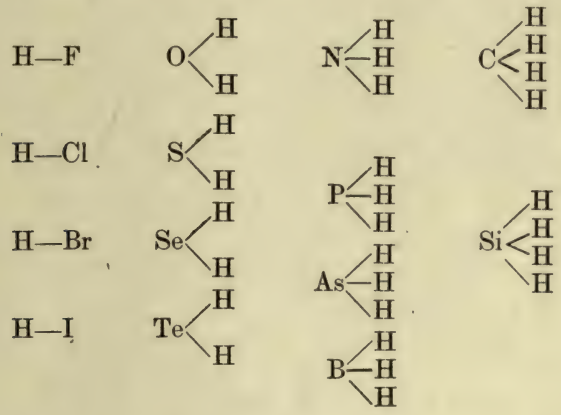
VALENCY OF THE ELEMENTS.

16 In connection with the non-metallic elements it has already been shown (vol. i., p. 126) that the atoms of these elements differ in the number of hydrogen atoms with which they can combine. This varying combining power of the elements is known as *valency* or *quantivalence*, and the elements are described as monovalent, divalent, trivalent, or tetravalent,

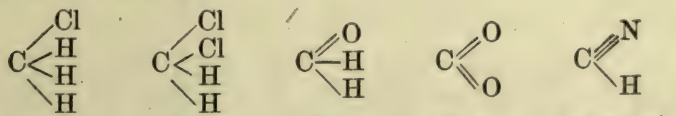
[1] *Pogg. Ann.* 1868, **135**, 337, 517.

[2] Ramsay, Collie and Travers, *Journ. Chem. Soc.*, 1895, i. 696.

or as monads, dyads, triads, or tetrads, according as they combine with one, two, three, or four atoms of hydrogen. This is also expressed by saying that each of these elements has one, two, three, or four *bonds* or *units of affinity*, and in combination with hydrogen each of these is satisfied by combining with the single unit of affinity of the latter. This is graphically expressed in the following formulæ, the mutual bond of affinity being represented by the straight line connecting the two atoms:



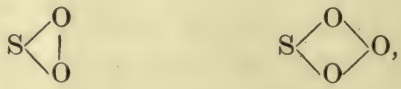
The further investigation of the non-metallic elements has shown that similar relationships are to be found in their compounds with elements other than hydrogen. Thus in the compounds mentioned above the hydrogen may be replaced by other elements and it has been found that those elements which combine with only one atom of hydrogen are only able to replace one atom of that element, whilst the divalent elements are able to replace two atoms, the trivalent three and so forth. Thus if we take the compound of carbon and hydrogen, CH_4, we can replace one or more atoms of hydrogen by an equal number of chlorine atoms, two or four atoms by one or two atoms of oxygen, and three atoms by an atom of nitrogen, the graphic formulæ of the compounds obtained being given below:—



Methyl chloride. Methylene chloride. Formaldehyde. Carbon dioxide. Hydrocyanic acid.

From these and many other similar facts, the conclusion was at first drawn by some chemists that the valency of an element is a constant property and remains the same in all compounds which it forms. As the number of the compounds whose true molecular weight was ascertained became larger, it was found, however, that this view could not be maintained without modification. Thus phosphorus, which forms the hydride PH_3, forms two chlorides PCl_3 and PCl_5, and as, in the latter, it is combined with five monovalent atoms it must in this case be pentavalent, whilst in PCl_3 and PH_3 it is trivalent. Upholders of the theory of constant valency denied that phosphorus pentachloride was a true compound, and regarded it as a *molecular compound* of PCl_3 and Cl_2, analogous to a salt containing water of crystallisation, basing this supposition on the fact that when phosphorus pentachloride is volatilised it decomposes into these two portions. It was then shown that by suitable means the pentachloride may be volatilised without decomposition, and that its vapour density then corresponds with the formula PCl_5, and further a phosphorus pentafluoride has been since discovered which is gaseous at the ordinary temperature and has the molecular formula PF_5. The valency of phosphorus towards the halogens cannot therefore be regarded as constant.

Again the two chief oxides of sulphur have the formulæ SO_2 and SO_3, and on the assumption that sulphur and oxygen are both divalent the constitutional formulæ were written :—

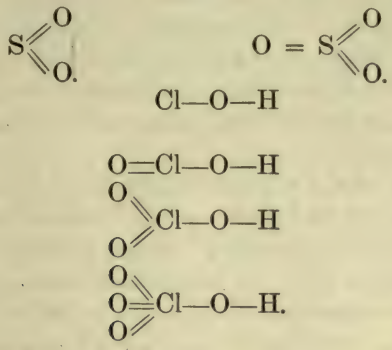


and among the oxygen compounds of chlorine we are acquainted with four oxy-acids having the formulæ $HClO$, $HClO_2$, $HClO_3$, and $HClO_4$, the constitution of which was represented as follows :—

H—O—Cl
H—O—O—Cl
H—O—O—O—Cl
H—O—O—O—O—Cl.

In all these cases, however, another interpretation is possible namely, that the divalent oxygen is connected directly with the sulphur or chlorine atom, the valency of the latter

varying in the different cases, as shown in the following formulæ :—



No definite proof has hitherto been obtained of the correctness of either view, but the balance of evidence is strongly in favour of the latter, as it is found that those compounds which can be proved to contain oxygen atoms directly combined together in the manner shown in the first series of formulæ, such as hydrogen peroxide, are extremely unstable compounds. It is, moreover, probable that the longer the chain of oxygen atoms, the less would be the stability of the compound, whereas in reality, the stability of the oxy-acids of chlorine increases with the number of oxygen atoms in the molecule. It is now, therefore, generally supposed that the valency of an element is not a constant, but a variable property.

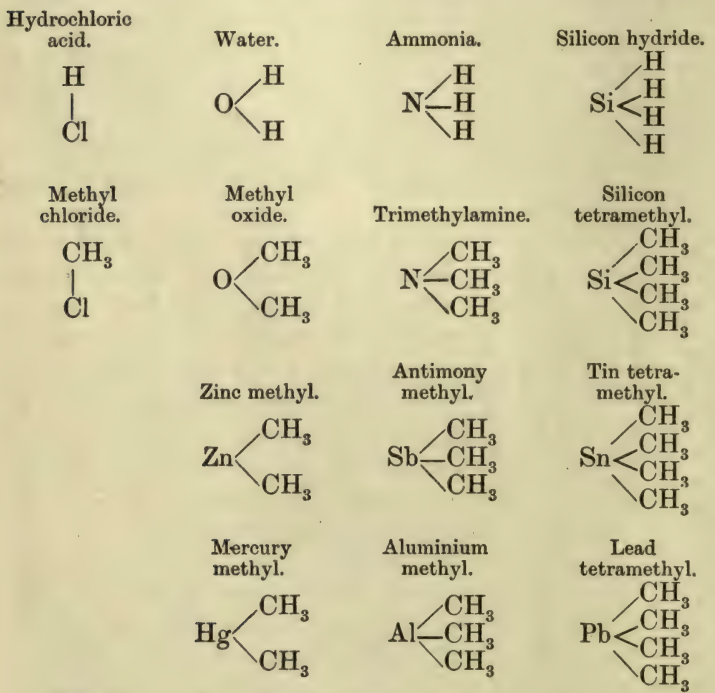
It will however be noticed that in the above cases there is a certain regularity in the variation, the valency of an element being always represented by either an odd or even number, and in the great majority of the compounds of the non-metallic elements the same rule is found to hold. Even to this, however, there are a few notable exceptions, such as nitric oxide, NO, in which nitrogen behaves as a dyad instead of as a triad or a pentad, whilst in chlorine peroxide, whose formula has been proved[1] to be ClO_2, chlorine is a tetrad, and in carbonic oxide, CO, carbon appears as a dyad.

17. When we consider the compounds of the metals, it is found that the relations become more complex than is the case with the non-metals. It is only in recent years that any very definite conclusions could be drawn on this point, as until then the true molecular weight of very few metallic derivatives was known,

[1] Pebal and Schacherl, *Annalen*, 1882, **213**, 113.

these having for the most part such high boiling points that the vapour density of very few of them had been determined. The improved methods of determining vapour densities at high temperatures, due chiefly to Victor Meyer and his pupils,[1] have however considerably enlarged the material at our disposal, and the results have necessitated some modification of the older views.

Scarcely any of the metals combine with hydrogen to form volatile compounds, and their valency towards this element cannot therefore be determined. Many metals, however, form volatile compounds with the monovalent alcohol radicals (p. 13), which may be regarded as metallic hydrides in which the hydrogen atoms have been replaced by alcohol radicals, and these also serve for the determination of the valency of such metals as form them. The table below gives the constitutional formulæ of some of the compounds of non-metals with hydrogen and alcohol radicals and of a number of the metallo-organic compounds of which the vapour density has been ascertained :—



[1] *Pyrochemische Untersuchungen*, 1884. (Vieweg); and numerous papers, *Ber.* 1880–1890.

Almost all the metals combine with chlorine, forming chlorides, and the vapour density of a number of these, together with that of a few iodides, has now been determined, the molecular formulæ of which are given below:

I.	II.	III.	IV.	V.	VI.
KI	$BeCl_2$	$AlCl_3$	$TiCl_4$	$NbCl_5$	WCl_6
RbCl	$CrCl_2$	$CrCl_3$	VCl_4	$TaCl_5$	
CsCl	$FeCl_2$	$FeCl_3$	$GeCl_4$	$MoCl_5$	
CsI	Cu_2Cl_2	$GaCl_3$	$SnCl_4$	WCl_5	
AgCl	$ZnCl_2$	$InCl_3$	$ZrCl_4$		
InCl	$GaCl_2$	$SbCl_3$	UCl_4		
TlCl	$SnCl_2$	$BiCl_3$			
	$InCl_2$				
	$HgCl_2$				
	$PbCl_2$				

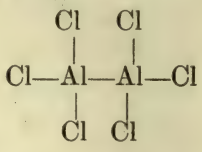
18 A definite conclusion as regards the molecular formula of a compound can only be drawn from its vapour density when the latter remains constant through a considerable range of temperature, as it is found in many instances that the vapour density of the compound diminishes gradually with increase of temperature, and only attains a constant value at temperatures considerably above the boiling point. The same fact has been observed with substances boiling at quite low temperatures, as, for example, acetic acid. In consequence of this, a single determination of the vapour density has led to incorrect conclusions with regard to the formulæ of several chlorides. Thus the first determination of the vapour density of ferric chloride, made by V. and C. Meyer,[1] agreed approximately with the formula Fe_2Cl_6, and this was therefore believed to be correct. Subsequently V. Meyer and Grünewald[2] showed that the vapour density of ferric chloride is, even at 448°, rather less than corresponds to the formula Fe_2Cl_6, and that as the temperature rises the density gradually becomes less, until at 750° the value closely agrees with the formula $FeCl_3$, and remains constant at that value up to 1,077°.

At temperatures above 448° a certain amount of the ferric chloride is dissociated into ferrous chloride and chlorine, but at 448° no decomposition of this character takes place and even here the vapour density is smaller than that required by the formula Fe_2Cl_6; hence at temperatures not far above the boiling

[1] *Ber.* 1879, **12**, 1, 195. [2] *Ber.* 1888, **21**, 687.

point, a number of the molecules must have a smaller molecular weight than the above, *i.e.*, they must have the formula $FeCl_3$.

Another instance of a similar kind has been observed in the case of aluminium chloride; the older experiments of Deville and Troost in 1857 gave the vapour density at 9·3, corresponding to the formula Al_2Cl_6, and this compound was, therefore, represented by the formula:



in which aluminium is regarded as a tetrad. Nilson and Petterson,[1] in repeating this determination in 1887 at higher temperatures, obtained the following numbers:

Temperature.	Vapour density.
440°	7·789
758°	4·802
835°	4·542
943°	4·557
1,177°	4·269
1,244°	4·247
1,260°	4·277

The calculated value for the formula Al_2Cl_6 is 9·2, and for $AlCl_3$ 4·6.

Further examples of this change of density are found in the case of stannous chloride and ferrous chloride; in both of these cases the density at low temperatures is variable, being lower than that required by the doubled formulæ Sn_2Cl_4, Fe_2Cl_4, although higher than that needed by the simpler formulæ $SnCl_2$, $FeCl_2$; at higher temperatures, however, a constant value corresponding to the simpler formula is obtained. Chromic chloride has been likewise proved to have the formula $CrCl_3$, and the double formulæ so long employed for the ferric, chromic, and aluminium salts must therefore now be abandoned.

An instance of an opposite character occurs in the case of cuprous chloride. The vapour density of this compound was found by V. and C. Meyer to correspond to the formula Cu_2Cl_2 at a bright red heat, and a later determination made at a white heat led to the same formula.

[1] *Zeit. Physik. Chem.* 1887, **1**, 463.

The constitution of cuprous and cupric chlorides may be represented by the formulæ:

Cuprous Chloride.	Cupric Chloride.
Cl—Cu—Cu—Cl.	Cl—Cu—Cl.

copper being regarded as a dyad in both cases. Mercurous and silver chlorides are undoubtedly analogous compounds to cuprous chloride and might be represented as follows:

Mercurous Chloride.	Silver Chloride.
Cl—Hg—Hg—Cl.	Cl—Ag—Ag—Cl.

The vapour density of mercurous chloride was, however, found to correspond to the simpler formula HgCl, from which it appeared that mercury is a monad in the mercurous compounds. The supporters of the theory that mercury is always a dyad, refused to accept the vapour density determination as a proof of the simpler formula, and suggested that the molecules Hg_2Cl_2, like those of ammonium chloride, do not exist in the gaseous form, but split up on volatilization into mercury and mercuric chloride, which reunite on cooling:

$$Hg_2Cl_2 = Hg + HgCl_2$$

If this decomposition were complete the observed vapour density would be identical with that required by the formula HgCl. Harris and V. Meyer[1] have shown that such a dissociation does in reality take place, for if the vapour of calomel is passed through a porous tube, mercury diffuses through the latter and condenses in globules, whilst the portion which finally condenses inside the tube contains an excess of mercuric chloride; and further if solid potash is placed in the vapour it is immediately coated with yellow mercuric oxide, and does not show even a momentary formation of the dark mercurous oxide. The vapour density cannot therefore be taken as a proof of the molecular formula HgCl, but on the other hand it in no way proves the existence of Hg_2Cl_2 molecules, and the true formula is therefore still doubtful.

The vapour density of silver chloride has also been determined by Biltz and V. Meyer[2] and though as might be

[1] *Ber.* 1894, **27**, 1482; 1895, **28**, 364. [2] *Zeit. Phys. Chem.* 1889 **4**, 249.

expected, the numbers obtained at the high temperature necessary for the determination (1735°) are not very exact, they are sufficient to indicate that the molecular formula is AgCl and not Ag_2Cl_2.

The examination of the list of chlorides shows that not only the valency of the same element does vary in different compounds, but that it does not even vary in a regular manner, such as remaining either odd or even. Thus in the case of indium, three volatile chlorides are known, having the formulæ InCl, $InCl_2$, $InCl_3$, in which the metal is a monad, dyad, and triad respectively. Iron is a dyad in ferrous chloride, and a triad in ferric chloride, whilst tungsten acts both as a tetrad, a pentad and a hexad.

In considering the compounds of the metals with oxygen, the available material is not so copious, inasmuch as the actual molecular weights have been determined in but few cases, and in most instances the formulæ of the oxides (and of the salts they form with either acid or basic oxides) are taken as the simplest possible, or in some cases as analogous to those of the oxides of elements of the same group whose vapour density has been determined. The valency deduced from these formulæ frequently differs from that obtained from the vapour density of the chloride of the metal; thus the only volatile chloride of vanadium has the formula VCl_4, whilst in its general deportment this element is analogous to nitrogen and phosphorus, behaving as a triad and pentad. Again, the only volatile chloride of molybdenum has the formula $MoCl_5$, but in many other compounds such as molybdic acid and the molybdates the metal acts as a hexad.

19 The valency of an element can no longer therefore be regarded as always varying in a regular manner, but appears to vary irregularly according to the nature of the other elements with which it combines. At the same time an element almost always shows what may be termed a characteristic valency, *i.e.*, a valency which remains constant throughout a large and important series of compounds. Thus, for example, the alkali metals are monovalent in the great majority of their compounds, although a few halogen derivatives have recently been prepared in which they behave as triads and pentads; the metals of the alkaline earths almost always behave as dyads, and nitrogen, phosphorus and arsenic either as triads or pentads. Carbon in particular shows a very constant tetrad

valency, almost the whole of its immense number of compounds containing the element in the tetravalent state. These general regularities find their best expression in the periodic classification of the elements and will be further considered in discussing the latter (p. 50).

Concerning the nature of valency very little is at present known. One important relation has, however, been established. When a salt of a metal is dissolved in water and the solution electrolysed, the amount of the metal which is deposited in a given time depends on the valency which the metal possesses in that particular salt. Thus when solutions of mercurous and mercuric nitrates derived from the same amount of nitric acid are electrolysed by the same current, twice as much mercury is liberated from the mercurous as from the mercuric salt, the same amount of oxygen being liberated in both cases. Since the same amount of electricity has been conveyed by the ions of mercury in the two cases, it follows that the electrical charge conveyed by each mercuric ion is twice as great as that conveyed by a mercurous ion. The same relation is found to be true in other cases, and it may be stated as a general law that the electrical charge which can be conveyed by an ion of a metal in the electrolysis of a solution of a salt is directly proportional to the valency of the element in that salt.

CLASSIFICATION OF THE ELEMENTS.

20 The number of substances at present described as elementary is about seventy (see list vol. i., p. 52), and of these about sixty have been subjected to close investigation and their properties and those of their compounds definitely ascertained. Their atomic weights have also been determined with a high degree of accuracy, and it has been shown that these numbers really represent atomic weights and not simply the equivalents of the elements. (See pp. 13–28.)

The question naturally arises whether these substances are in reality incapable of further decomposition or whether by suitable means they might not in turn be resolved into still simpler substances; and very soon after the enunciation of Dalton's atomic theory, speculations as to the compound nature

of the so-called elements were published. Thus in the year 1815 Prout[1] suggested that the elements were in reality all composed of hydrogen, basing his supposition on the numbers at that time adopted for the atomic weights compared with hydrogen, which were in most cases whole numbers. The extreme simplicity of the hypothesis attracted many adherents, but the later careful determination of the atomic weights by Berzelius did not confirm it. It was somewhat modified by Dumas,[2] inasmuch as he assumed that the unit weight of hydrogen was itself composed of two or even four atoms, in which case the atomic weights would all be multiples of either 0·5 or 0·25. The very careful experiments of Marignac and especially of Stas (p. 10) which were carried out with extraordinary care for the purpose of ascertaining the truth of Dumas's hypothesis, have conclusively shown that the atomic weights of many elements are multiples neither of 1, nor of 0·5, nor of 0·25.

Although Prout's hypothesis has not been confirmed, the enquiries made to investigate its validity brought to light a number of relationships which exist between the atomic weights of analogous elements. Even before the enunciation of the atomic theory and before the true nature of the alkalis and alkaline earths was known, Richter[3] had pointed out that the quantities of the alkaline earths, which all neutralised the same weight of an acid, could be arranged as members of the arithmetical progression a + nb, in which the value of n was 0 for alumina, 1 for magnesia, 3 for lime, 9 for strontia, and 19 for baryta. In 1817 Döbereiner called attention to the fact that the atomic weight of strontium is the mean of that of the two closely allied elements calcium and barium, and later on the same was found to be approximately true in the case of other groups of three elements or *triads* as they were called. In 1850 Pettenkofer brought forward the view that the atomic weights of analogous elements form members of an arithmetic series: thus, using the whole number nearest to the atomic weight, the following series were given:

[1] Anonymously published in Thomson's *Annals of Philosophy*, 1815, vol. vi., "On the Relations between the Specific Gravities of Bodies in their Gaseous State and the Weight of their Atoms."

[2] *Ann. Chim. Phys.* 1859, [3], **55**, 129.

[3] *Ueber die neuern Gegenstände der Chymie* 1797, **8**, 21.

	Difference.		Difference.
Li = 7		O = 16	
	16		16
Na = 23		S = 32	
	16		3 × 16
K = 39		Se = 80	
			3 × 16
		Te = 128	

and it was supposed that in the case of analogous elements the difference in the atomic weights is either a constant or a simple multiple of that constant. This idea was further developed by Kremers, Gladstone, and especially by Dumas, and attention was drawn to the analogy existing between such a group of elements and the homologous hydrocarbon radicals. Thus if we take the radicals of the $C_nH_{2n}+1$ and C_nH_{2n} series we have:

	Difference.		Difference.
CH_3 = 15		C_2H_4 = 28	
	14		14
C_2H_5 = 29		C_3H_6 = 42	
	14		14
C_3H_7 = 43		C_4H_8 = 56	

When the more exact modern numbers are employed, it is found that the differences between the atomic weights of the elements are not quite so regular as when the above approximate numbers are taken, but even then the approximation to Pettenkofer's rule seems far too close to be due to chance. Further investigation showed that a very large number of the elements could be divided into groups showing similar relationships, and in 1864, Lothar Meyer[1] tabulated a large number of such groups and arranged a certain number of the elements in the order given in the table on p. 40, according in the first place to the magnitude of their atomic weights, and in the second place to their valency.

Natural Arrangement of the Elements.

21 The discovery of any system which should embrace the whole of the elements was only rendered possible by the adoption of the consistent atomic weights proposed by Cannizzaro in 1858, and previous to this date all the attempts at classification con-

[1] *Die modernen Theorien der Chemie*, 1864, 1st Edition, p. 137.

—	Tetrad.	Triad.	Dyad.	Monad.	Monad.	Dyad.
	—	—	—	—	Li = 7·03	(Be = 9·3?)
Difference =	—	—	—	—	16·02	14·7
	C = 12·0	N = 14·04	O = 16·00	F = 19·0	Na = 23·05	Mg = 24·0
Difference =	16·5	16·96	16·07	16·46	16·08	16·0
	Si = 28·5	P = 31·0	S = 32·07	Cl = 35·46	K = 39·13	Ca = 40·0
Difference =	$\frac{89·1}{2}$ = 44·55	44·0	46·7	44·51	46·3	47·6
	—	As = 75·0	Se = 78·8	Br = 79·97	Rb = 85·4	Se = 87·6
Difference =	$\frac{89·1}{2}$ = 44·55	45·6	49·5	46·8	47·6	49·5
	Sn = 117·6	Sb = 120·6	Te = 128·3	I = 126·8	Cs = 133·0	Ba = 137·1
Difference =	89·4 = 2 × 44·7	87·4 = 2 × 43·7	—	—	71 = 2 × 35·5	—
	Pb = 207	Bi = 208	—	—	(Tl = 204?)	—

sisted in their division into groups, but did not bring out the relations which exist between them as a whole. This was first

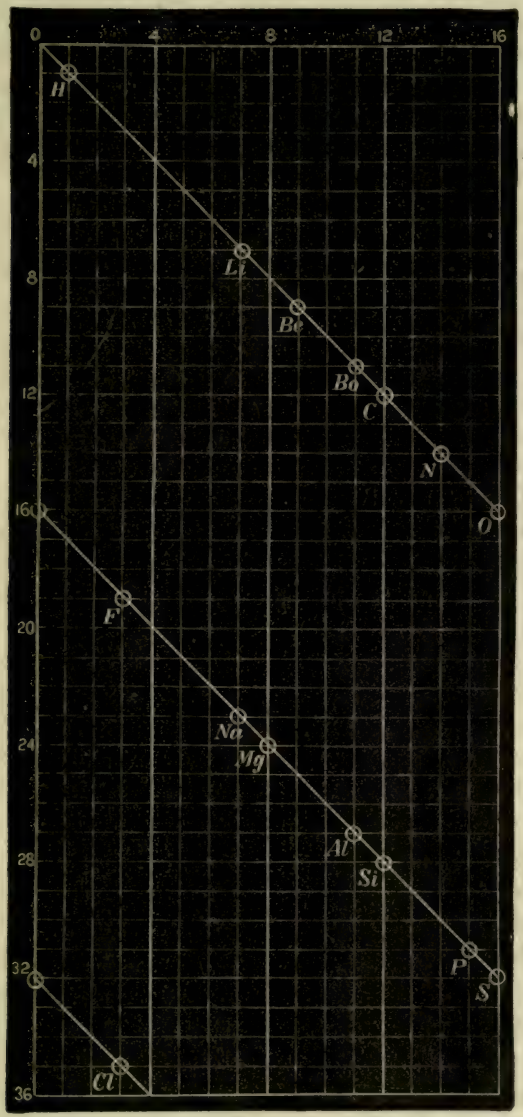


Fig. 1.

achieved in what is usually known as the *natural arrangement of the elements.*

The first attempt at such an arrangement was made by de Chancourtois[1] in 1862, in whose system the elements were arranged in order of their atomic weights along a spiral line drawn round a vertical cylinder, the surface of which was divided into sixteen vertical strips by straight lines. The points occupied by the various elements on this surface were termed "characteristic points," or "geometrical characters." De Chancourtois enunciated the fundamental theorem of his system as follows:—"The relations between the properties of different bodies are manifested by simple geometrical relations between the positions of their characteristic points. For instance, oxygen, sulphur, selenium, tellurium, and bismuth,[2] fall approximately on the same vertical generating line, while magnesium, calcium, iron, strontium, uranium and barium, fall on the opposite generating line. On either side of the first of these lines we find hydrogen and zinc on the one hand, bromine, iodine, copper, and lead on the other; parallel to the second line we find lithium, sodium, potassium, manganese, &c."

On p. 41, Fig. 1, will be found the representation of the first two turns of de Chancourtois' helix, the surface of the cylinder being developed on the plain surface of the paper, and it will be seen that the elements which lie on the same generating line do belong to the same family.

22 Very shortly afterwards (1864) several similar attempts at a classification of the elements as a whole, were made independently by Newlands,[3] who arranged the elements in order of their atomic weights, and finally placed them in seven horizontal series, each consisting of eight members, as shown in the following table:

H	F	Cl	Co, Ni	Br	Pd	I	Pt
Li	Na	K	Cu	Rb	Ag	Cs	Os
Be	Mg	Ca	Zn	Sr	Cd	Ba	Hg
B	Al	Cr	Y	Ce	U	Ta	Tl
C	Si	Ti	In	Zr	Sn	W	Pb
N	P	Mn	As	Di	Sb	Nb	Bi
O	S	Fe	Se	Rh, Ru	Te	Au	Th

[1] *Compt. Rend.* 1862, **54**, 757, 840, 967; 1862, **55**, 600; 1863, **56**, 263, 479; 1866, **63**, 24; see also Hartog, "A First Foreshadowing of the Periodic Law," *Nature*, 1892, **41**, 186.

[2] Probably a misprint, as bismuth does not fall on the same line in the table.

[3] *Chem. News*, 1864, **10**, 59, 94; 1865, **12**, 83, 94; 1866, **13**, 113, 130. See also Newlands *On the Discovery of the Periodic Law*, 1884. (E. and F. N. Spon.)

According to Newlands, the properties of an element in any vertical group are analogous to those of the elements in the corresponding position in the other groups. From analogy with the musical notes he gave to the hypothesis the name of the "Law of Octaves."

Both of these proposals, however, received very little attention on the part of chemists, indeed they seem to have been almost entirely forgotten. In fact, a systematic arrangement of the elements according to their atomic weights appeared to some chemists almost as absurd as the proposal of an alphabetical arrangement of the elements as a natural one would be. In the year 1869, however, the same system of classification, but on a wider basis, was proposed by the Russian chemist Mendeléeff,[1] without any previous knowledge of the work of the above named chemists. His classification not only included the elements then known but also left room for many elements at that time undiscovered. He showed that when the elements are arranged in order of their atomic weights, they may be divided into groups, in each of which a similar gradation of properties from element to element occurs, the properties of the elements thus appearing as periodic functions of the atomic weights.

At a slightly later date Lothar Meyer,[2] continuing his investigation of the relations between the elements, which had already led to the publication of the table given on p. 40, independently put forward views which were almost identical with those of the Russian chemist, and it is to these two investigators that the chief developments of the natural classification of the elements are due.

The Periodic System.

23 In his original paper,[3] Mendeléeff sums up his conclusions as follows:

(1). The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

(2). Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (*e.g.* platinum, iridium, osmium), or which increase regularly (*e.g.* potassium, rubidium, cæsium).

[1] *Zeitschr. Chem.* 1869, 405; *Annalen* Suppl. 1872, **8**, 133.

[2] *Annalen*, Suppl. 1870, **7**, 354.

[3] *Journ. Russ. Chem. Ges.* 1869, **1**; quoted in Faraday Lecture, *Journ. Chem. Soc.* 1889, 634.

Group.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
				MH_4	MH_3	MH_2	MH	Hydrogen cpds.
Series 1	H							
„ 2	Li 6·98	Be 8·99	B 10·74	C 11·91	N 13·94	O 15·88	F 18·9	
„ 3	Na 22·87	Mg 24·2	Al 26·9	Si 28·2	P 30·8	S 31·82	Cl 35·19	
„ 4	K 38·85	Ca 39·7	Se 43·8	Ti 47·6	V 50·8	Cr 51·7	Mn 54·6	Fe 55·6 Ni 58·6 Co 59·4
„ 5	Cu 63·1	Zn 64·9	Ga 69·4	Ge 71·8	As 74·4	Se 78·5	Br 79·36	
„ 6	Rb 84·8	Sr 87·0	Y 88·0	Zr 90·0	Nb 93·5	Mo 95·2	—	Rh 102·0 Ru 103·0 Pd 104·7

„ 7	Ag 107·13	Cd 111·3	In 112·8	Sn 118·2	Sb 119·4	Te (?) 124·0	I 125·91			
„ 8	Cs 131·9	Ba 136·4	La 137·5	Ce 139·0	Di (?)	—	—	—	—	—
„ 9	—	—	—	—	—	—	—			
„ 10	—	—	—	—	Ta 181·0	W 182·6	—	Os 189·3	Ir 191·7	Pt 193·3
„ 11	Au 195·7	Hg 198·9	Tl 202·6	Pb 205·4	Bi 206·4	—	—			
„ 12	—	—	—	Th 230·7	—	U 237·6	—	—	—	—
	M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_4	Highest salt forming oxides.	

(3). The arrangement of the elements, or of groups of elements in the order of their atomic weights corresponds to their so-called *valencies* as well as, to some extent, to their distinctive chemical properties—as is apparent, among other series, in that of lithium, beryllium, boron, carbon, nitrogen, oxygen, and fluorine.[1]

(4). The elements which are most widely diffused have *small* atomic weights.

(5). The *magnitude* of the atomic weight determines the character of the element just as the magnitude of the molecule determines the character of a compound body.

(6). We must expect the discovery of many yet *unknown* elements, *e.g.* elements analogous to aluminium and silicon, whose atomic weights would be between 65 and 75.

(7). The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

(8). Certain characteristic properties of the elements can be foretold from their atomic weights.

In the table given on pp. 44, 45, the elements are arranged according to the system of Mendeléeff and Lothar Meyer, and it will be seen that they fall into eight groups, each group occupying one of the vertical columns in the table, whilst there are twelve horizontal series or periods. The members of each group show in most cases a close connection with each other, which is most noticeable in the case of elements belonging to alternate horizontal series. In the table, therefore, the elements in each group are arranged on alternate sides of the column, each group becoming thus divided into two sub-groups, the members of one of which are situated in the horizontal series characterised by an *even* number, whilst the others fall in the *odd* series. Thus in the second group we have the two sub-groups Be, Ca, Sr, Ba, situated in the even horizontal series, and Mg, Zn, Cd, Hg, in the odd. The eighth group occupies a somewhat anomalous position, as it appears only to occur in the even periods or series, and unlike the other groups always contains three members, the atomic weights of which are more nearly equal than is usually the case with the other elements.

An inspection of the table shows that the first group contains

[1] Barium and iron are printed by mistake in the English original (*loc. cit.*) instead of boron and fluorine.

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all the alkali metals, the second group those of the alkaline earths, and also the metals beryllium, magnesium, zinc, cadmium, and mercury. In the third group we find the family aluminium, gallium, and indium; in the fourth carbon, silicon, titanium, zirconium, and tin; in the fifth nitrogen, phosphorus, vanadium, arsenic, antimony, and bismuth; in the sixth oxygen, sulphur, selenium, and tellurium; and in the seventh the halogens. The eighth group includes, in addition to the closely allied metals, iron, nickel, and cobalt, the whole of the elements known as the platinum metals. In almost all of these cases, the elements mentioned had been classed as members of the same family before Mendeléeff's work was published, and their continued occurrence in the same group is strong evidence in favour of the general correctness of his views.

On the other hand, cases will be observed in which there is no very evident connection between members of the two subgroups comprised in the same group, as for example in the case of silver, copper, and gold on the one hand, and the alkali metals on the other in the first group; a considerable number of resemblances can indeed be traced, but these are not so prominent as to have previously led to these elements being classified together. In the sixth group also there is very little obvious connection between chromium, molybdenum, and tungsten on the one hand, and the elements of the sulphur group on the other, nor in the seventh group between manganese and the halogens. It will, however, be noticed that in all these cases the elements which show deviations of this kind, come either just before or just after the occurrence of the eighth group of elements, and it is probable that their somewhat abnormal behaviour is in some way connected with the existence of this group.

Mendeléeff has suggested a second method of tabulation which overcomes certain of these difficulties (p. 48). The elements forming the first two periods, *i.e.*, those having the lowest atomic weights, and which in many respects differ from the members of the same groups having higher atomic weights, are regarded as typical elements, and the remainder of the elements are arranged in double periods, each consisting of an odd and even series of the first table. Comparing the two "typical" periods with the following long or double periods, it will be seen that the elements both at the beginning and at the end of the latter, present well-marked analogies

Natural Arrangement of the Elements. Second Table.

	H							
(1)	Li	Be	B	C	N	O	F	} Typical Periods.
(2)	Na	Mg	Al	Si	P	S	Cl	
(3)	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br	} Double Periods.
(4)	Rb	Sr	Y	Zr	Nb	Mo	—	Rh	Ru	Pd	Ag	Cd	In	Sn	Sb	Te	I	
(5)	Cs	Ba	(La	Ce	Di)	—	—	—	—	—	—	—	—	—	—	—	—	
(6)	—	—	—	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	
(7)	—	—	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	—	

Even series in table, p. 44–5. Eighth group in table, p. 44–5. Odd series in table, p. 44–5.

with the corresponding elements in the typical periods. Thus for example, K, Ca, Sc, Ti, and V at the beginning, and Zn, Ga, Ge, As, Se, and Br at the end of the first long period are closely analogous with the corresponding elements of the typical periods 1 and 2. On the other hand, the elements in the centre of the long periods, in this case Cr, Mn, Fe, Ni, Co, and Cu show either very little or no analogy with the typical elements. A comparison between the first two double periods (Nos. 3 and 4 in the table, p. 48), which contain only one space to be filled by a missing element, shows the very complete analogy which exists between them. In the later double periods so large a number of the elements is at present missing that the relations are not so apparent, although in many cases they are still distinctly seen.

As the atomic weight becomes higher, the change of properties in passing from any element to the one with the next highest atomic weight becomes less marked, and among those having the highest atomic weights, considerable resemblance is frequently noticed between two successive elements. Thus gold in many properties resembles both platinum and mercury, and lead is nearly related to thallium on the one hand and bismuth on the other.

A large number of the gaps in the later periods will doubtless be filled by the metals of the rare earths, but at present there is considerable doubt as to the exact atomic weights of most of these, and no attempt has been made to place most of them in the above table.

Chemical Properties in Relation to the Periodic System.

24 The periodic variation of both physical and chemical properties as we pass from group to group must now be considered, taking first the chemical properties.

The most strongly electropositive elements known, whose oxides act almost exclusively as bases or at most as neutral substances, occur in the first two groups (table, pp. 44 and 45), whilst the strongly electronegative elements, whose chief oxides form strong acids, occur in the sixth and seventh groups. The third, fourth, and fifth groups occupy an intermediate position, the members of the third group yielding oxides which, with the exception

of those of the elements having the lowest atomic weights, have for the most part basic properties, but frequently act as acids towards stronger bases; in the fourth and fifth groups the acidic nature of the oxides is most prominent in the case of the members of lower atomic weight, whilst the higher members show an increasing tendency to form basic oxides. Those members of the sixth and seventh groups which fall in the centre of the double periods form both basic and acidic oxides, the acid-forming oxides being those containing the most oxygen, and generally corresponding in formula with the acid-forming oxides of the other elements of the same vertical group. The members of the eighth group usually form basic oxides, but the highest oxides of ruthenium and osmium are strong acid-forming oxides.

Valency.

25 It has already been stated that the valency of an element cannot be regarded as constant, but that it varies according to the nature of the elements with which combination occurs. There is nevertheless, in general, a regularity in the valency of the elements in the majority of their compounds, and we usually speak of them as monovalent, divalent, &c., according to their behaviour in the most characteristic of their compounds. This typical valency shows in a marked manner a periodic variation with the atomic weight.

Thus the first group contains the whole of the metals which are usually monovalent towards the halogens, and the alkyl radicals, and also to oxygen, the typical formulæ of the compounds being $M^{I}R$ ($R = CH_3$, Cl, etc.) and $M_2^{I}O$. The metals of the second group act in most cases as divalent elements towards the halogens and alkyl radicals, and also to oxygen, the typical formulæ being $M^{I}R_2$ and $M^{II}O$. In the third group we find the metals which are usually trivalent in their compounds both with hydrogen or its equivalents and with oxygen, the typical formulæ of these being $M^{III}H_3$ and $M_2^{III}O_3$; and in the fourth we have the general formulæ $M^{IV}H_4$ and $M^{IV}O_2$, but in addition compounds are formed by these elements having the same general formula as those of Group II. In all these cases it is found that among the members having the highest atomic weights the regularity is less marked; thus gold is more frequently trivalent than monovalent, mercury and thallium

both form compounds in which the metal is monovalent, and lead in its most characteristic compounds is divalent.

Passing on to the fifth group it is found that the characteristic valency in the hydrogen compounds differs from that in the oxygen compounds, the members being trivalent in the hydrides and pentavalent in the highest oxides, the general formulæ being $M^{III}H_3$ and $M_2^{V}O_5$. They also form characteristic compounds with oxygen in which the metal is trivalent, and behave towards the halogens in the same manner as towards oxygen. In the sixth group the characteristic valency again becomes less towards hydrogen, the typical formula being $M^{II}H_2$, whilst with oxygen they form the characteristic acid-forming oxides $M^{VI}O_3$, and with halogens the compounds $M^{VI}Cl_6$. With oxygen and halogens they form in addition compounds having the same general formulæ as those of the elements of Groups II. and IV. The members of the seventh group are, like those of the first, monovalent towards hydrogen, but they are heptavalent towards oxygen in their highest oxides, which have the general formula $M^{VII}{}_2O_7$. Many of them also form oxides corresponding to those of the first, third, and fifth groups.

In the eighth group no very characteristic valency is noticeable, but it is only in this group that oxygen compounds containing an octovalent element are found; only two of these are at present known, namely RuO_4 and OsO_4. A characteristic of many members of this group is the formation of complex cyanides, such as the ferrocyanides, in which the metal is contained in the acid radical, and also of the remarkable series of compounds derived from ammonia, such as the cobaltammonium and platinammonium salts.

Physical Properties of the Elements in Relation to the Periodic System.

26 As with the chemical properties, so it is found that almost all the physical properties of the elements are periodic functions of the atomic weight.

(1) Specific Gravity and Atomic Volume.

One of the most characteristic properties of the elements is their specific gravity in the solid or liquid state, which has been

determined with considerable accuracy in the majority of cases. The following table gives the most reliable determinations of the specific gravity at the ordinary temperature.

SPECIFIC GRAVITY OF THE ELEMENTS.

Aluminium	2·56	Mercury (liquid)	13·59
Antimony	6·72	Molybdenum	8·6
Arsenic	5·67	Nickel	8·8
Barium	3·85	Niobium	6·27
Beryllium	1·64	Osmium	22·48
Bismuth	9·82	Palladium	11·5
Boron	2·68	Phosphorus (yellow)	1·83
Bromine (liquid)	3·18	„ (red)	2·11
Cadmium	8·6	Platinum	21·5
Caesium	1·88	Potassium	0·875
Calcium	1·58	Rhodium	12·1
Carbon (amorphous)	1·57	Rubidium	1·52
„ (graphite)	2·01–2·08	Ruthenium	12·26
„ (diamond)	3·5 –3·6	Selenium	4·3 –4·5
Chlorine (liquefied)	1·44	Silver	10·42–10·53
Chromium	6·8	Silicon	2·49
Cobalt	8·5 –8·9	Sodium	0·97
Copper	8·8 –8·9	Strontium	2·54
Gallium	5·9	Sulphur	1·8–2·14
Germanium	5·47	Tantalum	10·8
Gold	19·3–19·5	Tellurium	6·25
Indium	7·42	Thallium	11·9
Iodine	4·95	Thorium	11·1
Iridium	22·4	Tin	7·29
Iron	7·7 –8·1	Tungsten	19·2
Lead	11·38	Uranium	18·7
Lithium	0·59	Vanadium	5·5
Magnesium	1·74	Zinc	6·86–7·2
Manganese	7·4	Zirconium	4·15

The value often varies slightly with the same element not only with the temperature, but also with the physical condition. Thus cast metals or metals deposited electrolytically become denser when rolled and hammered, electrolytic copper having a sp. gr. of 8·952, which rises to 8·958 when rolled, and cast

zinc a sp. gr. of 6·9, whilst that of rolled zinc is 7·2. The different allotropic modifications of the same element also have as a rule rather different specific gravities, but in all these cases the difference is usually small compared with the differences between the numbers for the different elements.

The periodic variation of the specific gravity at once becomes manifest if the numbers are placed under the symbol of the element in the periodic table. Thus, taking the second typical period and first double period, we have the following :—

	Na	Mg	Al	Si	P	S	Cl
Sp. gr.	0·97	1·74	2·56	2·5	2·0	1·9	1·4

K	Ca	Se	Ti	V	Cr	Mn	Fe	Ni	Co
0·87	1·6	3·8	—	5·5	6·8	7·4	7·9	8·8	8·7

Cu	Zn	Ga	Ge	As	Se	Br
8·8	7·0	5·9	5·5	5·6	4·4	3·1

The specific gravity is low at the beginning of both periods, increases regularly to a maximum in the middle, and then decreases until it has again become very low at the end of the periods. It has already been noted that the difference between the atomic weights of the successive elements forming the centre of the double period is smaller than the average, and it will be observed that the variation of specific gravity is also less for these elements.

27 These relations become more strongly marked if, instead of the specific gravity, we take the atomic volume of the elements. This is obtained by dividing the atomic weight by the specific gravity, and the numbers, like the atomic weights themselves, are simply relative; they represent, however, the number of cubic centimetres which would be occupied by the atomic weight of the elements in grams. If these are arranged, as suggested by Lothar Meyer, so that the ordinates represent the atomic volumes and the abscissæ the atomic weights, and the points denoting the atomic volumes then joined, we obtain a line[1] which exhibits the periodic relations in a graphic manner.

[1] Mendeléeff points out that the use of this diagram has the theoretical objection that it does not indicate that there is only a limited and definite number of elements in each period, but might be taken to imply that any

This diagram is shown on p. 55 up to and including cæsium; after this metal the number of gaps due to incompletely investigated or missing elements becomes so large that the diagram is very incomplete, and this portion has therefore been omitted.

It will be seen that the atomic volume reaches a maximum at the commencement of each of the two typical periods, and then at the commencement of the double periods, falling to a minimum at the middle and then again rising to the end of the period, and from the last member of each period a further rise is observed to the initial member of the next. This diagram, moreover, brings out other relationships which are not otherwise so readily perceived. Thus elements whose atomic volumes are very nearly equal possess very different properties according as they are on an ascending or a descending portion of the line, or, in other words, according as they have a smaller or larger atomic volume than the element having the next higher atomic weight. This is exemplified in the cases of aluminium and phosphorus, chlorine and calcium, molybdenum and cadmium, &c. Elements which are characterised by the properties of ductility and brittleness always occur in corresponding positions in the curve diagram, the ductile elements being found at a maximum or minimum, or immediately following the latter. The periodic variation in these properties is clearly indicated in the table.

(2) Melting-Point of the Elements.

28 Another characteristic property of most elementary substances is the melting-point, although this has not been accurately determined in the case of so many elements as the specific gravity, chiefly owing to the difficulties of obtaining correct results in the case of those elements which melt either at a very high or a very low temperature. The following list gives the melting-points which have been most accurately

number of elements might occur in each period; thus, for example, it might be assumed that an element of atomic weight 25 might exist between Mg and Al, whose atomic volume would then be about 13, and whose properties would be intermediate between those of the two metals named; for such an inference there is in reality no ground, and it must therefore be borne in mind that the line joining the points representing the atomic volumes is not a true curve, such as, for example, those representing the solubilities of salts on p. 98, but is simply drawn to render the periodic variation more evident to the eye.

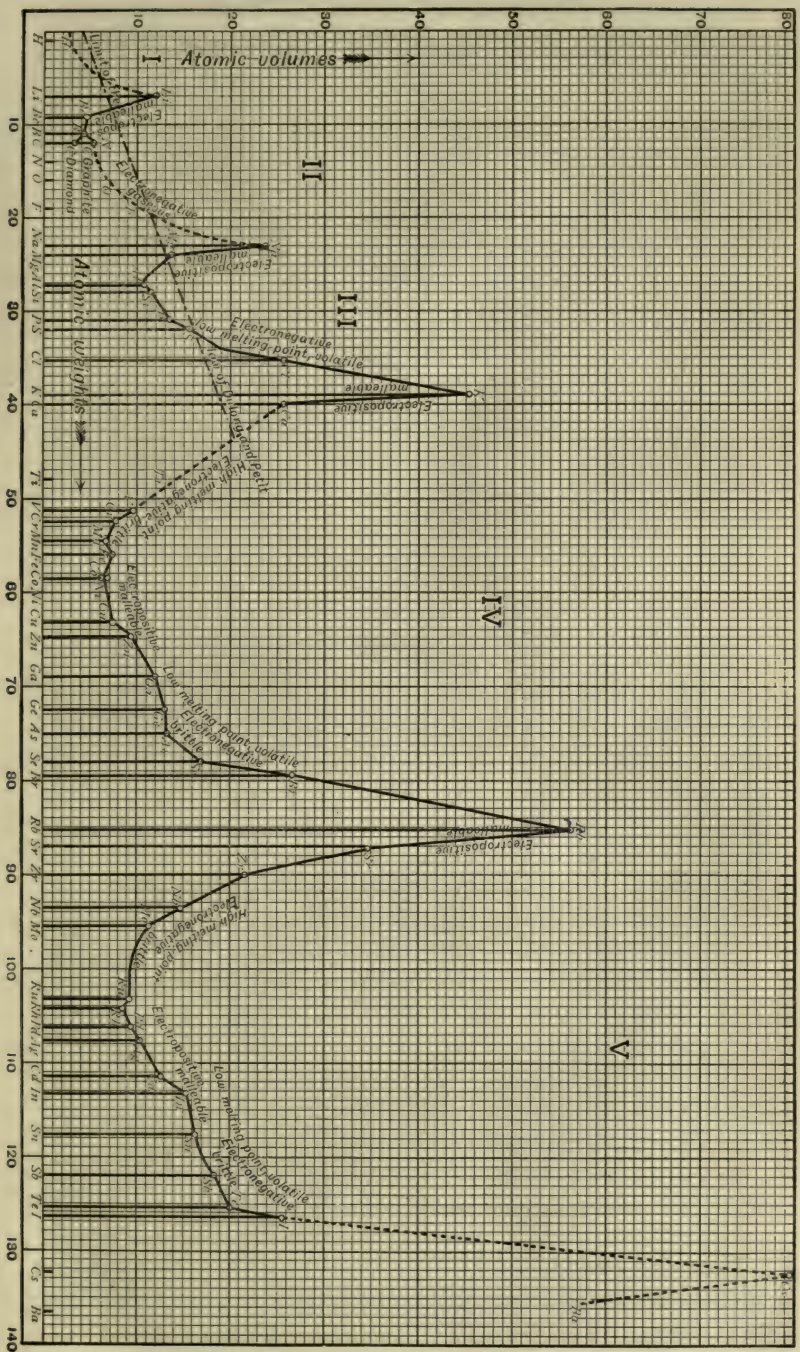


FIG. 2.—Lothar Meyer's Atomic Volume Diagram.

determined, and also the boiling-points where these are known:—

MELTING AND BOILING POINTS OF THE ELEMENTS.

	Melting point.	Boiling point.
Nitrogen	−214°	−194°
Chlorine	−102	− 33·6
Mercury	− 39·4	357
Bromine	− 7	59
Cæsium	26·5	—
Gallium	30	—
Rubidium	38·5	—
Phosphorus	44·3	290
Potassium	62·5	667
Sodium	95·6	744
Iodine	114·2	184
Sulphur	114·5	448
Indium	176	—
Lithium	180	—
Selenium	217	680
Tin	232	—
Bismuth	270	—
Thallium	282	—
Cadmium	320	770
Lead	326	—
Zinc	419	940
Arsenic	450	—
Tellurium	452	—
Antimony	629·5	—
Magnesium	632·7	—
Aluminium	654·5	—
Silver	960·5	—
Gold	1061·7	—
Copper	1080·5	—
Iron	1600 } about	—
Platinum	1775 }	

Carnelley has published a series of important papers,[1] containing an investigation of the relation between the melting-

[1] Published in *Journ. Chem. Soc.*, *Proc. Roy. Soc.*, and *Phil. Mag.* from 1876 onwards.

points and the atomic weights of the elements, and has shown that, like the specific gravities, these are also periodic functions of the atomic weight. This is readily seen from the following table (p. 58) taken from one of Carnelley's papers,[1] with some modifications of the numbers, rendered necessary by recent determinations of the melting-points of some of the elements. The numbers given are in many cases only approximate and all are given in absolute temperatures, taking $-273°$ C. as zero.

If the melting points are mapped out in the same manner as the atomic volumes, a similar curve is obtained, in which, however, the maxima occur in the centre of the second and third periods and afterwards in the centre of the double periods, whilst the minima occur at the ends.

Carnelley has further shown that the melting points of analogous compounds of the elements exhibit the same periodic variation with the atomic weights as those of the elements themselves.

(3) Conductivity of Metals.

29 The conductive power of the metals for heat and electricity, which is almost invariably far greater than that of the non-metals, and of all chemical compounds, also varies considerably in the individual metals, and even in the same metal, according to its physical condition and chemical purity. The order of conductive power of the metals is the same for both heat and electricity, a fact first pointed out by Forbes[2] in 1833. Generally speaking, the soft metals conduct best, and the conductivity of all metals becomes lower as the temperature increases. At low temperatures it becomes higher, and Liveing and Dewar have shown that as the temperature is lowered the conductivity of all metals tends to become more nearly equal, and the curves representing the conductivity at different temperatures indicate that at the absolute zero the conductivity of all of them would become perfect, or, in other words, at that temperature the resistance would be *nil*.

These properties, as well as almost all the other physical properties of the element, such as the volatility, magnetic and diamagnetic properties, thermal expansion, and even elasticity and breaking strain, indicate the same general periodic variation

[1] *Phil. Mag.* 1879, (5) **8**, 315. [2] *Phil. Mag.* 1833, **4**, 27.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
H							
< 40°							
Li	Be	B	C	N	O	F	
453°	< 1230°	v.h.	v.h.	59°	v.l.	v.l.	
Na	Mg	Al	Si	P	S	Cl	
369°	906°	928°	v.h.	yel. 317° red 528°	387°	171°	
K	C	Se	Ti	V	Cr	Mn	Fe Ni Co
335°	> Sr	?	v.h.	v.h.	> 2270°	2170°	1870° 1870° 2070°
Cu	Zn	Ga	Ge	As	Se	Br	
1353°	692°	303°	1170°	773°	490°	266°	
Rb	Sr	Y	Zr	Nb	Mo	—	Ru Rh Pd
311°	> Ba	?	> Si	v.h.	v.h.		2070° 2270° 1775°
Ag	Cd	In	Sn	Sb	Te	I	
1133°	593°	449°	505°	902°	725°	389°	
Cs	Ba	—	—	—	—	—	— — —
300°	v.h.						
—	—	—	—	—	—	—	
—	—	Yb	—	Ta	W		Os In Pt
		?		v.h.	v.h.		2770° 2220° 2050°
Au	Hg	Tl	Pb	Bi	—	—	
1335°	234°	558°	599°	543°			
—	—	—	Th	—	U	—	— — —
			?		> Fe		

v.h. = very high. v.l. = very low.

as has already been shown with the specific gravity and melting points; space will not permit the discussion of these here, but for details reference may be made to Lothar Meyer's "Modern Theories of Chemistry" translated by Bedson and Williams. (Longmans).

30 There is, however, one important physical property known which does not exhibit this periodic variation, viz., the atomic heat. As already shown (p. 16) this is approximately constant, and the fact is made use of in determining the true atomic weight of an element from its equivalent. A number of exceptions to this are however found, all of these being confined to elements of low atomic weight. These all fall below an oblique line drawn across Lothar Meyer's diagram from the commencement to the vertical line representing an atomic weight of 40 (see table p. 55) whilst those above the line follow the law. Or, without reference to the diagram, this may be expressed by saying that of the elements having an atomic weight of less than 40, only those follow Dulong and Petit's law at the ordinary temperature, whose sp. gr. in the solid state is greater than 1·5 or whose atomic volume is greater than 40.

Correction of Doubtful Atomic Weights.

31 The periodic arrangement of the elements has proved of great value in checking doubtful atomic weights. In 1869 when Mendeléeff first promulgated his theory, the atomic weights then accepted for many elements did not allow of their being placed in a position corresponding to their properties, and Mendeléeff boldly assumed that in such cases either the equivalent had been wrongly determined, or that an incorrect multiple of the latter had been taken for the atomic weight, and in almost every case subsequent research has justified his assumption. Thus, for example, the atomic weight of molybdenum was given by some chemists as 92 and by others as 96, and as the former number placed the metal before the pentavalent niobium, Mendeléeff adopted the number 96 which placed it in the same group as chromium: later determinations have given the number 95·2 (Liechti). The atomic weight of tellurium was then taken as 128, and this placed it after iodine, whereas it stands to iodine in the same relation as sulphur to chlorine and selenium to bromine, and must therefore have an

atomic weight of less than 126. The experiments of Brauner appear to show that this may be the case, but it is doubtful whether tellurium has yet been obtained pure. Again, the atomic weights of the four elements, gold, platinum, iridium and osmium were at that time taken as Au 195·2, Pt 195·7, Ir 195·7 and Os 197·6, whereas according to the requirements of the periodic system the order should be reversed, osmium having the lowest and gold the highest atomic weight; this also has been proved by the redeterminations made by Lothar Meyer and Seubert, Thorpe and Laurie, and Krüss, the numbers now adopted being Os 189·3, Ir 191·7, Pt 193·3 and Au 195·7.

The atomic weight of indium was at first taken as 75·2 and the formula of the chloride as $InCl_2$, but for an element of this atomic weight no place was available in the periodic system; if, however, the formula of the chloride be taken as $InCl_3$ the atomic weight becomes 112·8, and the element then falls naturally between cadmium and tin and in the same group as aluminium. Since then the determination of the specific heat of the metal and the vapour density of the chloride have proved the correctness of the supposition. Uranium also was formerly supposed to have an atomic weight 60 and later of 120, neither of these numbers fitting into the periodic system. The metal, however, falls in naturally if the atomic weight be about 240, and this was confirmed by the determination of the vapour density of uranium chloride, UCl_5, by Roscoe and by the determination of the specific heat of the metal by Zimmermann. Another element whose atomic weight was doubtful was beryllium, which was regarded by some as a divalent metal of atomic weight 9, and by others as a trivalent metal of atomic weight 13·5; the vapour density of beryllium chloride has now shown that this has the formula $BeCl_2$ and the atomic weight must therefore be 9, which agrees with the demands of the periodic system.

Existence of Unknown Elements.

32 The arrangement of the elements according to the periodic system leaves, as already seen, a number of blanks, which Mendeléeff assumed were to be filled by elements then undiscovered, and he suggested that from the properties of the elements with the next highest and lowest atomic weights, and

from those of the other elements in the same group it was possible to predict very closely the properties such an element would have when discovered. Thus for instance were selenium unknown, its properties could be largely predicted from those of arsenic and bromine on the one hand and of sulphur and tellurium on the other, these elements being termed by Mendeléeff the "atom analagons" of the element in question. At that time there were three gaps for elements with atomic weights less than 75, namely, one having an atomic weight of 44, corresponding to boron, one of atomic weight about 69, corresponding to aluminium, and one of atomic weight 72 corresponding to silicon. To these hypothetical elements Mendeléeff gave the names Ekaboron, Ekaluminium, and Ekasilicon (from the Sanskrit *Eka*, one), and proceeding in the manner indicated, he gave in considerable detail the properties such elements would possess. In less than twenty years his predictions were completely verified, by the discovery of gallium by Lecoq de Boisbaudran in 1875, of scandium by Nilson in 1879, and of germanium by Winkler in 1887. The first is Mendeléeff's ekaluminum, the second ekaboron, and the third ekasilicon, and the striking manner in which the forecast was fulfilled in each case may be seen from the following table, in which the predicted properties and those actually observed are arranged in parallel columns.

Ekaboron.	Scandium.
At. wt. 44.	At. wt. 44 (O = 16).
Oxide Eb_2O_3, sp. gr. 3·5.	Sc_2O_3, sp. gr. 3·86.
Sulphate $Eb_2(SO_4)_3$.	$Sc_2(SO_4)_3$.
Double sulphate not isomorphous with alum.	$Sc_2(SO_4)_3.3K_2SO_4$—slender prisms.
Ekaluminum.	**Gallium.**
At. wt. 68, sp. gr. 6·0	At. wt. 69·9, sp. gr. 5·96.

Ekasilicon.	Germanium.
At. wt. 72, sp. gr. 5·5.	At. wt. 71·8, sp. gr. 5·47.
Oxide, EsO_2, sp. gr. 4·7.	Oxide, GeO_2, sp. gr. 4·7.
Chloride, $EsCl_4$, liquid, boiling slightly below 100°, sp. gr. 1·9.	Chloride, $GeCl_4$, liquid boiling at 86°, sp. gr. 1·887.
Ethide, $Es(C_2H_5)_4$, liquid boiling at 160°, sp. gr. 0·96.	Ethide, $Ge(C_2H_5)_4$, liquid boiling at 160°, sp. gr. slightly less than water.
Fluoride, EsF_4, not gaseous.	Fluoride, $GeF_4.3H_2O$, white solid mass.

From the above it will be seen that the periodic system of classification rests on a very firm basis, the successful prediction of the properties of undiscovered elements forming very strong evidence in favour of the general plan. In certain respects the system will doubtless undergo modification as our knowledge increases, for difficulties occur which cannot at present be explained. Thus elements sometimes occur in the same group between which only a limited amount of analogy can be traced, and on the other hand elements which have a good deal in common are sometimes separated widely. The members of the higher periods often show considerable deviation in properties from the corresponding members of the lower periods, but when the very numerous gaps existing in the former shall have been filled up, and the elements at present only slightly known are more accurately investigated, these relations will probably become more plain.

A further difficulty is found in the anomalous position of hydrogen which forms the sole member of the first series at present known, and which in its properties differs to so great an extent from all other known elements. It resembles the alkali metals inasmuch as it is monovalent and strongly electropositive, but differs very greatly from them in other respects, and no satisfactory explanation of its isolated position has hitherto been forthcoming.

The recent discovery of argon will probably necessitate some modification of the present system, as at present there is no gap in which this can be placed. Various suggestions have been made for including it but until more is known of its chemical nature no definite conclusions can be drawn. In the case of helium, which appears to be probably a mixture of two

or more gases, the atomic weight of one at least of these must be less than that of lithium, and such elements must fall in the same horizontal series as hydrogen; the further investigation of this subject may, therefore, perhaps throw some light on the relation of hydrogen to the other elements.

CRYSTALLINE FORM OF METALS.

33 Most metals, as well as their alloys, can be obtained in the crystalline state, and those occurring as minerals in the native condition are often found crystallised; this is the case with gold, silver, copper, platinum, iridium, palladium, gold-amalgam, and silver-amalgam. In general the form which they assume is one belonging to the regular system, such as the octahedron or the cube, or a combination of these forms. Some few, such as zinc, antimony, and bismuth, crystallise in the hexagonal system, and the two latter metals, which closely resemble arsenic, are found, as this is, crystallised in rhombohedra. On the other hand, a few metals, such as tin and potassium, crystallise in the quadratic system.

To obtain metals in the crystalline state several processes can be adopted. Crystals of metals which fuse readily can be obtained by solidification after fusion. Bismuth, antimony, lead and tin may thus be crystallised, and in a similar way sodium and potassium; in the latter cases air must of course be excluded. Metals which are easily volatilised, such as zinc, cadmium, and potassium, may be obtained in crystals by condensation from the gaseous state, whilst other metals, such as silver, thallium, and lead, can be readily crystallised by the electrolysis of solutions of their compounds. The metals separate out in lustrous crystalline plates, and the exhibition of this phenomenon of crystallisation on the screen forms one of the most striking and beautiful of lecture-room experiments, and is also well illustrated by the formation of the lead-tree when a piece of zinc is immersed in a solution of lead acetate.

The fracture of metals is an important property intimately connected with the crystalline form, and in many instances it is of importance as giving a knowledge of the purity, or otherwise of the metal. The following varieties of fracture are generally recognised:—

(1). Crystalline fracture; as in antimony, bismuth, zinc, spiegel-iron, &c.

(2). Granular fracture; as in grey forged pig-iron.

(3). Fibrous fracture; as in bar and wrought iron when partly broken by bending.

(4). Silky fracture; as in a piece of tough copper.

(5). Columnar fracture; as observed in the grain tin of commerce.

(6). Conchoidal fracture; noticed in the cases of native arsenic and certain brittle alloys such as that composed of one part of copper to two of zinc (Percy).

ALLOYS AND AMALGAMS.

34 Especially characteristic of the metals as a class are the peculiar compounds or mixtures which different metals form with one another, and to which the name of alloy is given (derived through the French from the Latin *alligare*, to bind to). Amongst chemical compounds in general, those are found to be most stable and to show the greatest amount of chemical individuality whose constituents are the most diverse. In the case of the alloys, however, the essential properties of the metals are uniformly reproduced. Thus, they all possess metallic lustre; they conduct heat and electricity well, even when they assume distinct crystalline form and contain their constituents in the proportion of their combining weights. Hence alloys are distinguished from the compounds which the metals form with such elements as oxygen, sulphur, and chlorine, in which the general properties of the metal have undergone a complete change. So great indeed is the resemblance between the alloys and the metals proper that in all ages, in common parlance, they have been confused under the same name. The early Greek alchemists classed electrum, an alloy of gold and silver, amongst the metals, giving to it the sign of Jupiter, and even nowadays the word metal is often employed for designating an alloy.

35 The union of metals to form alloys may be brought about in three different ways:

(1) By fusing together the constituent metals.
(2) By strong compression of the finely powdered metals.
(3) By electro-deposition.

The first method is by far the most important of the three, as almost all alloys are produced in this way on the large scale. The second method has not received any, and the third only a limited technical application, and these may therefore be shortly discussed before passing on to the consideration of the first and chief method.

Compression.—The union of powdered metals to form alloys when strongly compressed was first observed by Spring,[1] who subjected the mixed powders to pressures up to forty tons per square inch in a steel cylinder, and in this manner obtained alloys identical with those obtained by fusion. It might be supposed that the union is in reality caused by the heat evolved during the compression causing the metals to melt; but Spring has shown that this is not the case, as if the whole of the work done in the compression were converted into heat, this would still be insufficient to effect the fusion of the mass.

Electro-deposition.—Just as copper can be deposited from solutions of its salts by electrolysis, so if we have a mixture of two metallic salts it is sometimes possible to deposit both metals simultaneously, so that they unite to form an alloy. Thus by electrolysing under suitable conditions a solution containing certain zinc and copper salts, brass is obtained.

Preparation of Alloys by Fusion.—The behaviour of the various metals when fused together has been examined by a number of chemists and metallurgists, especially by Matthiessen and more recently by Alder Wright, and it has been shown that whilst some metals form a homogeneous liquid when fused together in any proportion, others only do so when the relative proportions lie within certain limits. Alder Wright[2] has examined the whole of the alloys formed by the nine metals Pb, Bi, Zn, Al, Sn, Ag, Cu, Cd, Sb, numbering 502 in all, and the results of his investigation are summed up in the table on p. 66.

To distinguish from one another mixtures of metals which remain homogeneous whilst molten even on long standing, and mixtures which divide into two or more different fluid alloys, Alder Wright employs the terms "real" and "ideal" alloys.

The results obtained differ in many cases from those of pre-

[1] *Bull. Acad. Roy. Belg.* 1878, **45**, No. 6; 1880, **49**, No. 5; *Ber.* 1882, **15**, 595.

[2] *Proc. Roy. Soc.* 1889–1894; for summary of results see *Journ. Soc. Chem. Ind.* 1894, 1013.

vious observers, which is probably due to the latter not having allowed the molten metals to stand sufficiently long, as many of the mixtures are analogous to an emulsion, and only separate after a long period.

No. of metals in mixture.	Number of combinations possible.		Total.
	Constituent metals mixable together in all proportions so long as temperature is high enough to maintain fluidity.	Product divides into at least two immiscible alloys whose constituents are in proportions inside of certain limits.	
2	31	5	36
3	55	29	84
4	55	71	126
5	31	95	126
6	9	75	84
7	1	35	36
8	None.	9	9
9	None.	1	1
	182	320	502

Of the thirty-six binary alloys formed by taking the metals two at a time, it will be seen that thirty-one form real alloys and mix together in all proportions. In the following five cases separation into two distinct alloys takes place, unless the proportions are within certain limits: aluminium-bismuth, aluminium-cadmium, aluminium-lead, bismuth-zinc, and lead-zinc. Thus lead can only take up 1·6 per cent. of zinc, and zinc only 1·2 per cent. of lead.[1] Zinc on the other hand fuses with silver in all proportions, and these properties are made use of in the Parkes process of separating the small quantities of silver occurring in lead.

As the number of metals in the alloy increases, the proportion of "real" to "ideal" alloys becomes constantly smaller, as is seen from the foregoing table.

In the combination of fused metals, there is usually a slight evolution of heat; but in some cases, such as that of lead and

[1] Matthiessen and von Bose, *Proc. Roy. Soc.* 1862, **11**, 430.

tin, absorption of heat occurs. The thermal changes are however for the most part small, compared with those which occur in the combination of metallic and non-metallic elements, or of the latter among themselves.

36 *Liquation of alloys.*—When a homogeneous fluid alloy is cooled, it by no means necessarily follows that the solidified product is homogeneous throughout; in the majority of cases different portions of the solid are found to contain different proportions of the metals, and this phenomenon is known as *liquation.*

The subject of liquation was very carefully examined by Levol[1] in a series of researches, in the course of which he examined a large number of alloys. Among these were the alloys formed by copper and silver, and the only alloy of these metals in which no liquation is observed when the mass is quickly cooled is the one containing 71·89 per cent. of copper, which corresponds to the formula Ag_3Cu_2 and appears to be a true chemical compound. Roberts-Austen has shown that certain other silver-copper alloys, such for example as that used for the British silver coinage, containing 92·5 per cent. of silver and 7·5 per cent. of copper, exhibit scarcely any appreciable amount of liquation if allowed to cool slowly, although when quickly cooled this does take place to some extent.

Roberts-Austen has also examined the manner in which the temperature of a liquid alloy falls on cooling, the results being plotted in the form of a curve, and he has found that there are certain points at which the temperature remains constant for a short time and that these points occur nearly at the same temperatures, even when the percentage composition of the alloy is varied. It appears, therefore, that at these temperatures alloys of constant composition separate, which are, however, incapable of existing by themselves, but only in presence of an excess of one of the other metals.

From these results it appears that very few of the alloys are to be regarded as simple chemical compounds of the metals, but consist of intimate mixtures of two or more compounds of the metals, with, as a rule, an excess of one or more of the constituent metals. As already mentioned the alloy of copper and silver containing 71·89 per cent. of copper is a definite compound of the metals in atomic proportions, and amongst others the alloys of copper and zinc and copper and tin

[1] *Ann. Chim. Phys.* (3) 1852, **36**, 193; 1853, **39**, 163.

corresponding to the empirical formulæ $CuZn_2$ and SnCu, $SnCu_3$ and $SnCu_4$ also appear to be true compounds.[1]

The behaviour of the molten alloys, observed by Alder Wright, very closely resembles that of ordinary solutions; thus the metals which may be fused together in all proportions may be compared with solutions of water and alcohol, whilst those which form "ideal" alloys resemble water and ether, each of which can only take up a definite and limited proportion of the other. The liquation which takes place during the cooling of a molten alloy is further analogous to the behaviour of aqueous solutions of salts when gradually cooled until complete solidification ensues. Under these circumstances ice or the salt generally separates out at first, and later on frequently different hydrates of the salt, according to the temperature reached.

Roberts-Austen has further shown that metals diffuse into other metals just in the same manner as a salt in water. Thus a ball of gold immersed in a bath of molten lead at 550° diffused into the latter at a rate more than three times as great as that of sodium chloride into water at 18°; similar results have been obtained with gold in molten bismuth and tin, silver and lead in tin, &c. Moreover, diffusion takes place even in the case of solid metals, metallic gold contained in a cylinder of solid lead, slowly diffusing into the latter at temperatures at least as low as 100°, the rate of diffusion increasing with the temperature.[2]

Physical Properties of Alloys.

37 Certain of the physical properties of the metal are always preserved in the alloy. Thus, the specific heat and the coefficient of expansion of the alloy are always the means of those of its component metals. In other properties a variation takes place. Thus whilst the specific gravity of certain of the alloys is the mean of that of their constituent metals, that of others is always either greater or less than the mean specific gravity of the constituents. All alloys, with the exception of that formed by the union of one part of potassium to three of sodium, are solid at the ordinary temperature.

38 *Melting point of Alloys.*—The melting point of an alloy is usually lower than that of the metals which compose it.

[1] Roberts-Austen, *Phil. Mag.* 1879, (5), **8**, 551; Laurie, *Journ. Chem. Soc.* 1888, i. 104; Foerster, *Zeit. anorg. Chem.* 1895, **10**, 309.

[2] *Nature*, 1896, **54**, 55.

This is well seen in the case of ordinary plumbers' solder, consisting of tin and lead, which melts more easily than either of the metals composing it. This fact was known so long ago as the time of Pliny, for he states that tin cannot be soldered without lead, nor lead without tin, and that lead tubes are soldered with a mixture of one part of tin and two parts of lead, a mixture which is used at the present day. Homberg, in 1669, recommended an alloy of equal parts of tin, lead, and bismuth for sealing up anatomical preparations; and in 1772[1] Valentine Rose the elder discovered the well-known fusible metal which bears his name. This consists of one part of tin, one part of lead, and two parts of bismuth. It melts at 95° to 98°, the lowest melting point among the constituents being that of tin, viz., 232°. Another alloy, consisting of eight parts of lead, fifteen of bismuth, four of tin, and three of cadmium, softens at a temperature of 60° and is perfectly liquid at 65°, the melting points of its constituents being tin 232°, bismuth 270°, cadmium 320°, and lead 326°.[2] The proportions of the metals which yield an alloy of the lowest melting point do not however correspond to definite atomic proportions.[3]

Heycock and Neville have recently examined the effect on the melting point of a metal caused by the addition of small quantities of another metal, and have shown that in some cases a rise, and in others a fall takes place in the temperature of incipient freezing, *i.e.*, the temperature at which separation of solid commences. A rise is only observed in those cases in which the metals combine together chemically to form a compound having a higher melting point than that of the predominant metal (as in the case of antimony in tin or bismuth, and silver in cadmium). In the great majority of cases a fall is observed, which is proportional to the quantity of metal added and inversely to its molecular weight, and hence in this manner they have been able to obtain conclusions as to the molecular weight of the metal when dissolved in other metals, using the principle involved in Raoult's method of determining molecular weights (*see* p. 26, and vol. i., p. 114).

39 *Conductivity of Alloys.*—The conductivity of alloys for electricity was very carefully examined by Matthiessen in 1860, who found that they may be divided into two classes,

[1] *Stralsund Magazin*, 1772, 2.

[2] Lipowitz, *Dingl. Poly. Journ.* 1860, **158**, 376.

[3] Guthrie, *Phil. Mag.* 1884, (5), **17**, 462.

according to the way in which the conductivity varies with the composition.

In one of these, of which the alloys of tin and zinc are an example, the conductivity is the mean of that of the components, whilst in the other class, of which copper and zinc, and gold and silver, are examples, this is not the case, the conductivity being always less than the mean.

When the results are plotted in curves, breaks are also frequently observed, which, like the breaks in the cooling curves already mentioned, indicate the existence of alloys of definite composition at those points. Thus in the curve of silver and copper, a distinct break is observed for the alloy containing 71·89 per cent. of silver, which Levol (p. 67) had already shown to be a true atomic compound.

The conductivity of the alloys like that of the pure metals decreases with increase of temperature, and *vice versa*. The increase at low temperatures is however not so great as with the metals.

40 Many alloys can be obtained in well-developed crystalline forms, and this is not confined to such alloys as are true compounds. Thus Cooke[1] has shown that alloys of zinc and antimony, varying in composition from 43 to 64 per cent. of zinc, all crystallise in the same form, although in a different form from other alloys of these two metals. In the same way Matthiessen and von Bose[2] have observed, in the case of the gold-tin alloys, that well-defined crystals are not limited to definite proportions of the two metals, but are common to all alloys of these metals containing from 27 to 43 per cent. of gold. Storer[3] has likewise proved that all the copper-zinc alloys crystallise in the same form.

Most of the other physical properties of the alloys are different from those of the constituent metals, such as hardness, elasticity, tensile strength, &c. Thus wires of either silver, copper, tin, or zinc alone are lengthened by loads which would have scarcely any effect on a similar wire of their alloys, such as gun-metal and brass; pure gold and silver are too soft to be minted, but the addition of a small proportion of copper gives them the necessary hardness.

The solubility of alloys in acids also frequently differs from that of the metals forming them. If an alloy of platinum and

[1] *Mem. Amer. Acad. N.S.* **5**, 337.
[2] *Proc. Roy. Soc.* 1862, **11**, 433.
[3] *Boston. Amer. Acad.* **8**, 27.

silver be boiled with nitric acid it is completely dissolved, whereas platinum when unalloyed is quite insoluble in this acid. On the other hand, silver by itself readily dissolves in nitric acid, but it does not do so when it is alloyed with much gold, the whole of the silver being soluble only when its quantity is at least double that of the gold. It was formerly believed that in order to separate the whole of the silver only one quarter of the alloy must consist of gold, whence the term *quartation*, which is still used for the separation of these metals.

In certain cases, such as that of the copper-tin alloys containing excess of tin, it is possible by the action of hydrochloric acid to remove the excess of the latter, leaving sparingly soluble alloys of copper and tin having a definite composition corresponding to the formulæ, CuSn and Cu_3Sn.[1]

41 *Allotropic Modifications of Metals in Alloys.*—The addition of very small quantities of another element frequently brings about a great change in the properties of a metal, although, the quantity of the former added is too small to allow of the supposition that a true compound is formed. Thus, for example, the conductivity of copper is very greatly affected by the presence of extremely small percentages of foreign metals such as tin, and the hardness and tenacity of metals are also greatly altered by small quantities of other elements. Matthiessen was, therefore, led to the conclusion that when a metal is alloyed with small quantities of another, the former frequently undergoes a molecular change, and is converted into an allotropic modification showing very different properties. Thus the addition of 0·1 per cent. of tellurium to bismuth brings about a most remarkable change in the physical properties of the latter; moreover, as is well known, the physical properties of iron undergo remarkable alterations on the addition of varying quantities of carbon, and of other elements such as silicon, phosphorus, tungsten, &c. These changes are possibly due in part, at least, to such an allotropic change in the iron itself.

In connection with this subject Roberts-Austen has investigated the effect of the addition of small quantities of other metals to pure gold, and has shown that metals which diminish the tenacity and extensibility, have high atomic volumes, while those which increase these properties have either the same or a lower atomic volume. The elements

[1] Foerster, *Zeit. anorg. Chem.* **10**, 309.

which exert a deteriorating effect on gold occupy, therefore, a high position on Lothar Meyer's atomic volume diagram (p. 55), whilst those having little or no effect occur at the minima, and hence in this, as in so many other cases, the properties are a periodic function of the atomic weight.

Many of the alloys are largely employed in the arts and manufactures, as they possess properties which are wanting in the single metals. Pure copper is so soft and tenacious that it is not suitable for use in the lathe. The addition of half its weight of zinc produces the alloy brass, which is hard and yet possesses the necessary brittleness to enable it to be readily turned. Gun-metal is a very tenacious and hard alloy, containing nine parts of copper to one part of tin. A still harder alloy is bell-metal, consisting of two parts of tin to eight parts of copper. The more tin such an alloy contains the lighter is its colour. Speculum metal possesses a white colour, is capable of receiving a very high polish, and is, therefore, used for the specula of telescopes. It contains one part of tin to two parts of copper. Type-metal is made up of one part of antimony to four parts of lead. This alloy is hard, easily fusible, not brittle, and expands at the moment of solidification—properties which conjointly are possessed by no other single metal or alloy.

Amalgams.

42 Amalgams are compounds or mixtures of metals with mercury and, although really belonging to the class of alloys, are usually distinguished by this term. The name is first found in the writings of Thomas Aquinas; and Libavius explains the meaning of the word as follows:—"Amalgama corruptum vocabulum esse ex Graeco *μάλαγμα* non dubitant." It is perhaps more probable that the word is derived from the Arabic, as the form *algamala* also occurs in the writings of the alchemists.

The ancients were acquainted with the fact that mercury can combine with the metals, and they employed this property for the extraction of gold from its ores; Vitruvius even gives a method for extracting by means of mercury the gold from vestments which have been embroidered with gold thread. The Latin Geber speaks more distinctly respecting the compounds of the metals with mercury, for we find in his work,

Summa perfectionis magisterii, the following words, "Mercurius adhæret tribus mineralibus de facili, Saturno (lead) scilicet, Jovi (tin) et Soli (gold). Lunæ (silver), autem magis difficulter. Veneri (copper) difficilius quam Lunæ. Marti (iron), autem nullo modo, nisi per artificium. Est enim amicabilis et metallis placabilis. Solvuntur Jupiter et Saturnus, Luna et Venus ab eo." Thus it is clear that Geber knew that, with the exception of iron, mercury combines directly with all the metals. The problem of the preparation of iron amalgam was one to which the alchemists paid great attention as, according to Geber, it was no easy matter. Libavius gives the first hints towards the solution of this problem, as he says that the common metals require to be purified by corrosive action before they can be made to unite with mercury.

Amalgams are usually obtained by the direct union of the metal with mercury. In this case diminution of temperature is not unfrequently noticed, as when tin is dissolved in mercury. Sometimes, on the other hand, heat is evolved, as when the alkali-metals are amalgamated. Amalgams are also produced by the addition of mercury to a solution of a metallic salt; thus if this metal be added to a solution of silver nitrate, the amalgam separates out in splendid crystals—the *Arbor Dianæ* of the ancients. Another mode of obtaining an amalgam is to place the metal in a solution of mercuric nitrate, or together with mercury and a dilute acid; and lastly, amalgams are formed by the action of a weak galvanic current upon a solution of salt into which a globule of mercury has been poured, the zinc pole dipping into the globule of mercury.

The amalgams correspond in their chemical relationships to alloys, consisting generally of a mixture of one or more amalgams of definite composition with an excess of mercury; a much larger number of amalgams of definite composition has, however, been isolated than is the case with the alloys of any other metal. The amalgams containing a large quantity of mercury are often liquid, whilst those which contain less are frequently found to crystallise. When heated above the boiling point of mercury a number of the amalgams retain a certain proportion of mercury. Thus silver amalgam when heated to 450° leaves a compound which still contains 12 per cent. of mercury; and a gold amalgam treated in the same way leaves a residue containing 10 per cent. of mercury.[1]

[1] De Souza, *Ber.* 1875, **8**, 1616; *Ber.* 1876, **9**, 1050.

Similar results are obtained with copper, sodium, and potassium, the composition of the residues corresponding to the following formulæ:—

$$Ag_{13}Hg,\ Au_9Hg,\ Cu_{16}Hg,\ K_2Hg,\ Na_3Hg.$$

The two last are crystalline, and the sodium compound takes fire on exposure to the air. The metals lead, tin, cadmium, and bismuth do not retain mercury at a temperature of 450°.

Regarded as compounds the amalgams are very unstable, for Joule[1] has shown that they can be decomposed by subjecting them to a very high pressure.[2]

Many amalgams are used in the arts. Tin amalgam is employed in the silvering of mirrors, gold and silver amalgams in the processes of gilding and silvering in the dry way; zinc and tin amalgam for coating the rubbers of electrical machines, copper and palladium amalgam, and an amalgam of varying proportions of silver, copper and tin, sometimes with gold and platinum, for stopping teeth.

CONSTITUTION OF SALTS, ACIDS, AND BASES.

43 The word salt even at the present day is commonly applied to sea-salt or sodium chloride, and there can be little doubt that originally the term was given to the same substance, the Greek form of the word (ἅλς), in the feminine being used for the sea itself, whereas in the masculine it denoted the solid residue left when sea water is evaporated. The growth of the application of the word salt from a special to a generic term appears to have had its origin in the fact that just as common salt is obtained by the evaporation of sea-water, so other kinds of salt can be obtained by the evaporation of other liquids, as when, for instance, wood-ashes are boiled with water the clear solution yields on evaporation a white soluble residue to which the name of salt was applied. This extension of the term, as Kopp remarks, was, however, not accompanied by any knowledge of the differences between the substances thus classed together, exhibiting indeed ignorance with respect to the chemical differences

[1] *Mem. Manch. Lit. and Phil. Soc.* 1865, (3) **2**, 115.

[2] See also Dudley, *Proc. Amer. Assoc.* 1890, 145.

of these various soluble substances. Even up to the end of the last century the wider application of the word salt may be said to have been prevalent. Amongst the alchemistic writings of the earliest times the words salpetræ, salnitri, salmarinum, salarmoniacum, salvegetabile and the like occur; these bodies are all soluble in water and may be again obtained from solution by evaporation. The ideas connected with these salts were vague and indefinite. But a new meaning was afterwards given to the word salt, the term being applied to the solid bodies obtained by the combustion or ignition of substances. This view was upheld by Paracelsus, and was generally, though not universally, adopted by chemists. Thus we find in the seventeenth century that salt was considered to be one of the hypothetical essential constituents of all bodies, every substance being made up of salt, sulphur, and mercury (see Historical Introduction, vol. i., p. 7). The view that salt is an essential constituent of all bodies was strongly opposed by Boyle, who paid much attention to the investigation of salts, and to whom we owe much of our knowledge of the special nature of the different salts. He did not, however exactly define to what class of bodies the term salt ought to be applied. This was specially accomplished by Boerhaave, who in his *Elementa Chemiæ*, published in 1732, describes the special properties of salts to be their solubility, fusibility, or volatility, and taste, alkalis and acids being, according to this definition, also considered as salts. These were divided into salia alcalina, salia acida, salia salsa, salia media, salia neutra, and salia composita. Under the last named was understood a class of salts obtained by the union of an acid with an alkali or metallic calx. The chief characteristics of the salts still remained their solubility and peculiar taste. It was soon seen that such a definition leads to contradictions, for baryta, nitric acid, and sulphuric acid would thus be salts as well as nitrate of barium, whilst sulphate of barium, which is insoluble, and, therefore, possesses no taste, would not be a salt. Hence the necessity became obvious of separating alkalis and acids from the true salts, or salia media as they were called, and the word salt was now taken to mean such substances as are obtained when an acid and a base are brought together or when an alkali or metallic calx is neutralized by an acid.

44 Although acids and alkalis were included among the salts, chemists had long recognized that these substances are

characterized by special properties. The only acid known to the ancients was vinegar or acetic acid. Hence the name of this substance and the notion of acidity were represented by closely-related words (ὄξος, *acetus*, vinegar; ὀξύς, *acidus*, acid). The power of vinegar to produce an effervescence when brought on to the carbonate of an alkali was observed in early times.—Thus we read in Proverbs xxv. 20, "As he that taketh away a garment in cold weather, and as vinegar upon nitre, so is he that singeth songs to an heavy heart." Nitre in this case stands for natron or native carbonate of soda. It was also well known that vinegar acts as a solvent upon many substances, as in the celebrated story of Cleopatra dissolving pearls. The Arabians were acquainted with many other acids. The Latin Geber termed nitric acid *aqua dissolitiva*, and he gave the same name to the liquid obtained by strongly heating alum in a retort, which was probably dilute sulphuric acid. This shows that the special characteristic of an acid, according to the older alchemists, was its power of dissolving substances which are insoluble in water. Other properties common to the whole class of acids were not observed until a much later date. In 1668 Tachenius noticed that all acids are capable of combining with alkalis. Hence he considered silica to be an acid. Boyle[1] points out that the substances known as acids have the following properties. They are bodies which (1) act as solvents, but act with varying power on different bodies; (2) they precipitate sulphur and other bodies from their solutions in alkalis; (3) they turn blue vegetable colouring matter red, whilst alkalis bring the blue colour back again; (4) they can combine with alkalis, when the characteristic properties of each body disappear and a neutral salt is formed. These properties were henceforward regarded as the special characteristics of acids, and accordingly F. Hofmann in 1723 asserted that the *spiritus mineralis*, which exists in many mineral springs, and which we term carbonic acid, belongs to the class of acids as it turns blue litmus solution red. Thirty years later Black strengthened this conclusion by showing that this same substance possesses the power of destroying the caustic nature of the alkalis, giving rise to a distinct class of salts.

45 Such alkaline substances as lime, the potashes obtained by

[1] *Reflections upon the Hypothesis of Alcali and Acidum*, **4**, 284, and elsewhere.

the combustion of plants or by heating cream of tartar, and natron, or native carbonate of sodium, were well known to the Greeks, Hebrews, and Romans. To these was added the spirit of urine, which became known to the alchemists of the thirteenth century, but these substances were not generally looked upon as possessing the common property of alkalinity until the time of the iatro-chemists. These ascribed the various diseases of the body to the change in proportion between the acid and alkali in the various organs and fluids, and indeed sought to explain all the phenomena of chemical action as taking place between acids and alkalis. Some of the special characteristics of alkalis which were recognized about this time have already been mentioned in discussing the properties of the acids, and to these was added the power of effervescing with acids. The caustic alkalis which did not effervesce with acids were supposed to be more complex than the mild alkalis. Thus lime was supposed to acquire its caustic properties by taking up igneous particles from the fire in which the limestone was burned; when it was added to a mild alkali, these particles passed into the latter and rendered it caustic. This belief endured until Black in 1755 discovered the true nature of the phenomenon. The alkalis known at about the middle of the eighteenth century were the volatile alkali, and the two fixed alkalis, distinguished as the mineral alkali (soda) and the vegetable alkali (potash).

46 In the new system of chemistry, founded by Lavoisier after the overthrow of the phlogistic theory, the three classes of substances, acids, bases, and salts were for the first time clearly separated. The acids, distinguished by the properties already discussed, comprised the compounds of certain elements (the acidifiable bases) with oxygen, whilst the alkalis, earths, and metallic oxides possessed the common property of being able to combine with acids to form the third class of substances, the salts, in which the properties of alkalinity and acidity were alike wanting. The discovery of the compound nature of the alkalis by Davy, (1807) showed the justice of Lavoisier's classification, inasmuch as these substances were thereby proved to be, in fact, metallic oxides.

The view that all acids contain oxygen, to which this substance owes its name, was soon generally adopted. On the other hand, it was pointed out by Berthollet that prussic acid and sulphuretted hydrogen, which do not contain oxygen

act in many respects as acid bodies. Lavoisier's views, however, carried the day, it being assumed that the substances just mentioned really contained oxygen. The next step in the progress of our knowledge on this subject was Davy's investigations on chlorine and hydrochloric acid, carried out in 1808–1810, by which he proved that a powerful acid exists which certainly does not contain oxygen. Gay-Lussac's discovery of hydriodic acid, and the proof that prussic acid likewise contains no oxygen (1815) soon came in corroboration of this view. Acids were henceforth divided into two classes, the *oxy-acids* and the *hydracids*, whilst the salts derived from them were known as *amphid* salts (*ἀμφί*, both, since the acid radical and the base both contained oxygen) and *haloid* salts (*ἅλς*, sea-salt, *εἶδος*, like) respectively. The sulphides and selenides were afterwards included among the amphid salts because of the analogy of sulphur and selenium with oxygen. These elements were for this reason termed amphids, whilst the elements of the chlorine group, which combine directly with metals to form haloid salts, were termed haloids. The oxy-acids were the substances which we now term the acid-forming oxides, whilst those bodies which we now term the oxygenated acids were considered to be the hydrates of these oxy-acids.

The dualistic view that salts are formed either by the union of an acid with a metallic oxide, sulphide, or selenide, or by the direct union of a metal with a haloid element, received its most complete expression in the electrochemical theory of Berzelius.

The fundamental principle of this system was laid down by its author in the statement that "in every chemical combination there is a neutralization of opposite electricities, and that this neutralization produces heat in the same manner as it is produced by the discharge of a Leyden jar, without being in this latter case accompanied by an act of chemical combination." The application of this principle led to the view that "every compound substance, whatever the number of its constituent principles, may be divided into two parts, one of which is electrically positive towards the other. For example, sulphate of soda is not compounded of sodium, oxygen, and sulphur, but of sulphuric acid and soda, each of which can again be divided into two elements, one positive, the other negative. In the same way alum cannot be regarded as directly com-

pounded of its simple principles; it must rather be considered as the product of the reaction of sulphate of alumina, the negative element, on sulphate of potash, the positive element."[1] In accordance with this theory Berzelius wrote the formula for sodium sulphate $NaO + SO_3$, or in his contracted formulæ $\dot{N}a\ddot{S}$.

The amphid salts were thus looked upon as compounds of the second order, formed by the union of two oxides, each of which was a compound of the first order, formed from its elements. The haloid salts, on the other hand, such as KCl_2, were compounds of the first order.

47 At this time no distinction was made between what are now known as mono-, di- and tri-basic acids. Thus nitrate of potash was supposed to be formed in a precisely similar manner to the sulphate, and the formulæ of these two salts were accordingly written by Berzelius, $KO.N_2O_5$, and $KO.SO_3$, the atomic weight which was then adopted for potassium being twice that now in use. When two salts of the same acid and base were known, such as the sulphate and bisulphate of potash, it was supposed that the second salt was formed by the combination of the first with a second molecule of the acid, the formula of the second salt being therefore written $KO.SO_3 + H_2O.SO_3$ or $KO\,2SO_3$, the water sometimes being omitted.

The researches on the phosphates carried out by Graham in 1833 showed that this theory must be modified, since if trisodium phosphate contained only one atom of base the formula of phosphoric acid would become $P_{\frac{2}{3}}O_{\frac{5}{3}}$, which was incompatible with the atomic weights of phosphorus and oxygen as independently ascertained. Graham showed that the formation of the ortho-phosphates might be readily explained by supposing that phosphoric acid was capable of combining with three atoms of base, and that this base might be either water or a metallic oxide. He therefore formulated orthophosphoric acid and its sodium salts as follows (the modern equivalents of his formulæ being employed):

Orthophosphoric acid . .	$P_2O_5 + 3H_2O.$
Acid sodium phosphate. .	$P_2O_5 + 2H_2O + Na_2O.$
Ordinary sodium phosphate	$P_2O_5 + H_2O + 2Na_2O.$
Trisodium phosphate . .	$P_2O_5 + 3Na_2O.$

[1] Berzelius, *Traité de Chimie.*

The water in the first and second and third of these salts is essential to the composition of the salt, since when it is removed new salts are formed (vol. i., p. 590).

In 1838 Liebig published his important investigation on the constitution of the organic acids, in which he showed that many of the organic acids resemble phosphoric acid in their relations to bases. He further proposed that all acids which form mixed salts containing two different, non-isomorphous bases, should be considered as belonging to the same class as phosphoric acid. In this memoir, moreover, he discussed the question whether the salts and oxyacids are compounds of a metallic oxide or water with an acid-oxide, or whether all acids and salts may be represented as combinations of metals or hydrogen with some other element or group of elements. This view had been originally suggested by Davy and independently by Dulong (in 1816), but had not been generally admitted. The difference in constitution between the oxyacids and the hydracids necessitated a different explanation for reactions which are in fact similar. Thus, for instance, when hydrochloric acid acts upon zinc it was assumed that the metal simply replaced the hydrogen of the acid:

$$Zn + 2HCl = H_2 + ZnCl_2.$$

When, however, sulphuric acid acts upon zinc it was necessary to assume that the presence of the acid enables the zinc to decompose the water (predisposing affinity) in order that an oxide may be formed with which the acid can unite; the reaction was, accordingly, represented as taking place in two stages:

$$(1)\ Zn + H_2O = H_2 + ZnO.$$
$$(2)\ SO_3 + ZnO = SO_3,ZnO.$$

In the same way when hydrochloric acid reacts with lime, water is formed. On the other hand, when the same base combines with sulphuric acid no water is produced:

$$(1)\ 2HCl + CaO = H_2O + CaCl_2.$$
$$(2)\ SO_3 + CaO = SO_3,CaO.$$

Liebig pointed out that the new view does away with these inconsistencies and also with the distinction between hydracids and oxyacids, amphid salts, and haloid salts; acids being

regarded simply as hydrogen compounds, the replacement of the hydrogen in which by metals gives rise to salts. In Liebig's opinion the view is less applicable to inorganic than to organic compounds. Nor was it until certain facts became known which were favourable to this theory, that it was generally admitted that acids and salts possess an analogous constitution.

48 If aqueous hydrochloric acid be decomposed by an electric current, chlorine is evolved at the positive pole and hydrogen is liberated at the negative. If dilute sulphuric acid be treated in a similar way a simple decomposition of water apparently takes place, for at the positive pole we only obtain oxygen and at the negative pure hydrogen. The same phenomenon is observed in the electrolytic decomposition of a solution of sodium sulphate, but at the same time sulphuric acid is liberated at the positive pole whilst soda makes its appearance at the negative pole together with the hydrogen. Hence, in this case, it was argued that the current both decomposed the water into its elements and the salt into its immediate components. If a solution of sulphate of copper be subjected to the same treatment, oxygen is evolved at the positive pole and sulphuric acid liberated, whilst at the negative pole metallic copper separates out; this was explained by the supposition that the copper oxide which ought to be deposited is reduced to the condition of metal by the nascent hydrogen.

These phenomena were specially examined by Daniell.[1] It appeared to him important to determine the relation between the quantity of oxygen and hydrogen, on the one side, and of the acid and the alkali on the other, formed in the electrolysis of a salt of an alkali; and as the result of a large number of careful experiments he found that these several substances are produced in the proportion of their equivalents, and that this is true not only in the case of sodium sulphate, but also in the cases of other salts of the alkalis. Daniell also observed the remarkable fact that the same current which apparently is capable of producing these two decompositions is capable of liberating exactly the same quantity of hydrogen and of oxygen from dilute sulphuric acid. In this latter case, therefore, the current was apparently able to effect only half the work which it was capable of producing in the decomposition of an aqueous saline solution, because in this case not only the salt but, as it

[1] *Introduction to Chemical Philosophy*, second edition (1843), p. 533.

seemed, the water also, underwent decomposition. This is however clearly impossible, and the phenomena observed can be readily explained by assuming that in the decomposition both of aqueous sulphuric acid and of the solution of a sulphate, either hydrogen or a metal is liberated at the negative pole, whilst at the positive pole the group SO_4 is set free. But this cannot exist in the free condition, as it decomposes at once into oxygen and sulphur trioxide, the latter dissolving instantly with formation of sulphuric acid. When a salt of an alkali is decomposed, the metal which is liberated instantly decomposes the water with evolution of hydrogen. According to this view the electrolytic decomposition of the oxysalts is exactly analogous to that of the chlorides, and hence they must be similarly constituted. Daniell proposed a new nomenclature for the oxysalts:

H_2SO_4	Hydrogen oxysulfion.
Na_2SO_4	Sodium oxysulfion.
HNO_3	Hydrogen oxynitrion, &c.,

which has, however, never been generally adopted.

The further development of chemical theory has completely confirmed the view that acids and salts are strictly analogous, salts being derived from acids by the replacement of hydrogen by a metal. This analogy has received expression in the nomenclature employed by many chemists for these substances, according to which the acids are termed hydrogen salts. Thus, just as nitre is called potassium nitrate, nitric acid is called hydrogen nitrate, sulphuric acid hydrogen sulphate, &c. In 1851 Williamson pointed out that the basic oxides and hydroxides, the oxygen acids and the salts derived from them, might all be considered as derived from one or more molecules of water, by the partial or complete replacement of the hydrogen by other elements or groups. When the hydrogen of water is replaced by a metal, a basic oxide or hydroxide is produced, so that potash and anhydrous oxide of potassium have the formulæ $\frac{K}{H}O$ and $\frac{K}{K}O$. When on the other hand the hydrogen is replaced by chlorine or a group of atoms such as NO_2, ClO_3, SO_2, &c., acids are formed such as $\frac{NO_2}{H}O$, $\frac{(ClO_3)}{H}O$, $\frac{SO_2}{H_2}O_2$, &c., the remaining

[1] *Journ. Chem. Soc.* 1852, 350.

hydrogen of which can be replaced by metals with the formation of salts.

49 If we ask ourselves the question, What is the cause of the acid character of bodies? we may say that acids must contain hydrogen together with certain elements or groups of elements which are termed negative elements or groups, inasmuch as these separate out at the positive pole in the act of electrolysis. A compound may however contain these negative elements or groups of elements, and also hydrogen, and yet not belong to the class of acids. Hence it appears that the atoms or groups of atoms must be combined with hydrogen according to a particular plan in order that the compound may assume the character of an acid. Sir Humphry Davy,[1] in 1816, pointed out perfectly correctly, that it is impossible to assert that a particular body is an acid-forming or an alkali-forming principle, and that such a definition would be nothing more than to re-introduce *qualitates occultas* into science. The chemical properties of a body are, said Davy, determined by "the corpuscular arrangement" of the constituent particles.

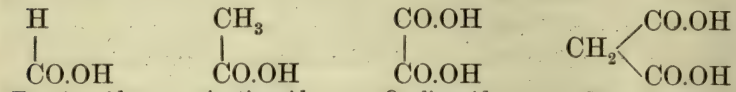
Amongst the different acids, the hydrogen compounds of the elements of the chlorine group possess the simplest constitution. They contain one atom of hydrogen combined with one atom of a powerful negative element. In the oxygen acids the hydrogen which can be replaced by metals is always found to be combined with oxygen in the form of the radical hydroxyl, OH; this is proved by the fact that these acids can as a rule be obtained by the action of water on the corresponding chlorides,

$$SO_2\begin{matrix}Cl\\Cl\end{matrix} + 2H_2O = SO_2\begin{matrix}OH\\OH\end{matrix} + 2HCl.$$

The ease with which the hydrogen of such a hydroxyl group can be replaced by a metal depends upon the nature of the group with which it is combined. This is well illustrated by many organic compounds, which assist us more than any other class in the solution of the problem as to what determines the acid nature of a compound. From a study of the organic acids it appears that when the OH group is combined with the group CO, the compound containing these groups is an acid, whilst when the OH group is united with the groups CH_2 or CH_3 the

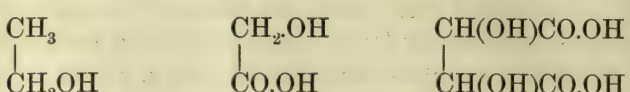
[1] *Jour. Sc. and Arts, Roy. Inst.* 1816.

compound is not an acid. Thus formic and acetic acids are monobasic acids, malonic and oxalic, dibasic acids:



Formic acid. Acetic acid. Oxalic acid. Malonic acid.

whilst alcohol, $CH_3.CH_2.OH$, is not an acid; hydroxy-acetic acid, which contains two OH groups, is nevertheless monobasic and tartaric acid, which contains four OH groups, is only dibasic:



Alcohol. Hydroxy-acetic acid. Tartaric acid.

The group SO_2 exerts a similar influence, so that such a substance as $C_6H_5.SO_2.OH$ is also found to be a strong acid.

A similar effect is produced by the presence of many groups in a molecule containing hydrogen which is not present in the form of the OH group. Thus, if one atom of hydrogen in ethane be replaced by nitroxyl, NO_2, we obtain the acid nitro-ethane which, when acted upon by bromine, a strongly negative element, is converted into bromonitro-ethane, $C_2H_4BrNO_2$, which is also a strong acid. If however a further atom of hydrogen in this compound be replaced by bromine, a perfectly neutral substance is obtained termed dibromonitro-ethane, $C_2H_3Br_2NO_2$. The constitution of these bodies is as follows:

$$\begin{cases} CH_3 \\ CH_2NO_2 \end{cases} \qquad \begin{cases} CH_3 \\ CHBrNO_2 \end{cases} \qquad \begin{cases} CH_3 \\ CBr_2NO_2 \end{cases}$$

It will be noticed that the presence of the groups NO_2 and Br does not render the hydrogen atoms of the CH_3 group replaceable by metals.

The four atoms of hydrogen of marsh gas can also be replaced by nitroxyl:

$$CH_3NO_2 \qquad CH_2(NO_2)_2 \qquad CH(NO_2)_3 \qquad C(NO_2)_4$$

The three first of these substances are acids, whilst the fourth is a perfectly neutral substance.

Although it is characteristic of all acids that they contain hydrogen which can be replaced by metals, all substances which fulfil this condition are not termed acids. Thus substances of such different properties as ammonia, NH_3, water, H_2O, and alcohol, C_2H_5OH, all yield metallic derivatives, NH_2Na, NaHO and C_2H_5ONa, when they are directly acted on by metallic sodium; whilst marsh gas, CH_4, and benzene, C_6H_6, can by indirect means be converted into organo-metallic derivatives such as $(CH_3)_2$ Zn, $(C_6H_5)_2Hg$. It is therefore usual to roughly define acids as compounds which contain hydrogen capable of being replaced by a metal when the latter is presented to them in the form of a hydroxide. It is however impossible to draw a hard and fast line between substances which are, and those which are not acids, since, especially among the organic compounds, the two classes pass imperceptibly into one another.

Constitution of Salts, Acids, and Bases in Dilute Solution.

50 As already explained (vol. i., pp. 116, 282) the behaviour of acids, bases and salts in dilute solution has led to the conclusion that these substances are to a large extent dissociated into electrically charged ions, and that during electrolysis these give up their electrical charges to the oppositely charged electrodes, the electricity being thus entirely conveyed by the ions of the substance. The products which are actually obtained by the electrolysis are not always the ions themselves, but are formed from them either by decomposition, combination or reaction with the water or some substance present in the solution. Thus when a solution of sodium chloride is electrolysed, the positive ion, or kation, Na gives up its charge to the negatively charged electrode and immediately acts on the water of the solution, liberating hydrogen, which escapes, and forming caustic soda, which remains in solution. On the other hand, the negative ion, or anion, Cl gives up its charge to the positively charged electrode and combines with a second atom of chlorine to form a molecule of chlorine gas which escapes. It will be observed from the preceding remarks that the charged ions have quite different properties from the substances in their ordinary state. Thus a charged sodium ion has no action on water, whereas so soon

as it loses its charge, it becomes capable of entering into reaction with the water as explained.

The extent of the dissociation may be measured by the depression of the freezing point of the water, as already described, provided that the molecular weight of the salt be known. Another method which may be employed for the same purpose is the measurement of the electrical conductivity of the solution. It is found that when a moderately strong solution of a salt, &c., is diluted, the conductivity per unit of dissolved substance increases, and, as the dilution proceeds, approaches a definite limit, which may be taken as the conductivity of the salt when dissolved in an infinite amount of water, so as to make a solution of infinite dilution. This is shown in the following table for solutions of potassium chloride. The numbers in the second column represent the relative conductivity for a fixed amount of the salt in solutions which contain m gram-molecules of the salt per litre, the values of m being given in the first column.

m	Conductivity.	Percentage of dissociated mols.
2	864	71
1	911	75
0·1	1,047	86
0·01	1,147	94
0·001	1,193	98
0·0001	1,209	99
Limit.	1,220	100

The percentage of dissociation in any given solution is then represented by the ratio of the actual conductivity of the substance in that solution to its conductivity in a solution of infinite dilution. The numbers of the third column in the table above show the amount of dissociation into two ions which occurs in the case of potassium chloride in the various solutions. The results obtained by this method agree generally with those obtained by the freezing-point method.

It has been found that what are called acid properties, are peculiar to substances of which one of the kations is hydrogen, whilst the anion OH is characteristic of basic substances. Weak acids and bases, such as acetic acid, boric acid, ammonia, &c., are found to be only very slightly dissociated, whilst strong acids and bases, such as hydrochloric and nitric

acids, caustic soda, and caustic potash are very largely dissociated even in moderately strong solution. The percentage of dissociated molecules in solutions which contain 1 gram-equivalent per litre of the various substances, is 60—90 for strong acids and bases, and 0—20 for weak acids and bases. The salts of weak acids moreover are dissociated to a much greater extent than the acids themselves.

The action of acids, bases and salts on the colouring matters known as indicators, such as litmus, phenol-phthalein, &c., receives a very interesting explanation in the light of this theory. The substances which are used as indicators are themselves either weak acids or weak bases, or salts derived from them. Thus blue litmus solution contains the sodium salt of a very weak acid, which, like most salts even of weak acids, is largely dissociated, the ions being the colourless kation $\overset{+}{\mathrm{Na}}$ and a complex anion which gives the liquid its blue colour. When an acid is added to the solution these complex anions are brought into the presence of free kations of hydrogen, with which they immediately unite to form molecules of the weak acid of litmus, which is much less dissociated than its sodium salt, and causes the liquid to appear red. The change of colour is therefore due to the fact that the molecule of the acid imparts to the solution a different colour from that given by the anion. It follows from the above that an acid indicator will only be sensitive to such acids as are more strongly dissociated than itself, since only acids which fulfil this condition will render possible the union of the anion of the litmus acid with hydrogen kations. Hence it is that the various indicators differ in their sensibility towards acids, and that some weak acids such as boric acid do not show an acid reaction towards litmus. In the same way methyl-orange is not affected by carbonic acid nor by sulphuretted hydrogen; properties of which advantage is taken in various methods of volumetric analysis. Similar considerations hold with regard to the reactions of basic substances. Thus when caustic soda is added to a solution of red litmus, the few free hydrogen ions of the litmus acid unite with the $\overset{-}{\mathrm{OH}}$ anions of the caustic soda forming water. Equilibrium being thus disturbed, a fresh number of the molecules of the acid undergo decomposition; the hydrogen ions thus liberated unite with the $\overset{-}{\mathrm{OH}}$ anions, and this process goes on until practically the whole of the molecules

of the acid have been dissociated; the corresponding number of molecules of water are formed and the solution finally contains kations of $\overset{+}{Na}$ together with the $\overset{-}{OH}$ anions of the caustic soda, and the anions of the litmus acid, which render the liquid blue.

Molecules which are capable of yielding more than two ions appear to undergo only a partial dissociation in aqueous solution. Thus for example, sulphuric acid, which is capable of yielding the three ions $\overset{+}{H}$, $\overset{+}{H}$, $\overset{--}{SO_4}$, is found in dilute solutions to be mainly dissociated into the two ions $\overset{+}{H}$, and $\overset{-}{HSO_4}$, whilst only a comparatively small proportion of the $\overset{-}{HSO_4}$ ions are further dissociated into $\overset{+}{H}$ and $\overset{--}{SO_4}$.

Some salts in which no replaceable hydrogen is present do not possess a neutral reaction when dissolved in water, whilst others containing replaceable hydrogen are not acid to indicators. Thus salts formed from a strong acid and a weak base, such as ferric chloride, chromic chloride, aluminium sulphate, &c., usually have an acid reaction, whilst on the other hand salts formed from a weak acid and a strong base have an alkaline reaction, as is seen in the case of sodium carbonate, sodium borate, sodium acetate, sodium nitrite, sodium aluminate, sodium silicate, &c. Moreover, disodium hydrogen phosphate Na_2HPO_4, $NaHCO_3$ and other similar acid salts are neutral or even alkaline to indicators. It seems probable that in such cases the salt is partially decomposed or hydrolysed by the water of the solution, in which it is to be supposed that there is always a certain number of free hydrogen and hydroxyl ions, although this number must be a very small one. Taking the example of a salt of a weak monobasic acid, such as nitrous acid or acetic acid, with a strong base such as caustic soda, we have the following relations. When sodium acetate is dissolved in water the following reaction probably occurs, between a few of the ions of the salt and the free ions of $\overset{+}{H}$ and $\overset{-}{OH}$ to which reference has just been made, molecules of the weak, slightly dissociated acid, $C_2H_4O_2$, being formed:

$$\overset{+}{Na} + \overset{-}{C_2H_3O_2} + \overset{+}{H} + \overset{-}{OH} = \overset{+}{Na} + \overset{-}{OH} + C_2H_4O_2.$$

As a result of this action there remains an excess of hydroxyl ions, and the solution has therefore an alkaline reaction.

Similar relations exist in solutions of many salts of weak acids, such for example as those of potassium cyanide which always smell of hydrocyanic acid. When the salt has been formed from a strong acid and a weak base, on the other hand, the hydrogen ions are present in excess and the solution has an acid reaction. Some salts which have been formed from both a weak acid and a weak base are completely decomposed in dilute solution. This is especially characteristic of the salts of the weak organic bases.[1]

METALLIC OXIDES AND HYDROXIDES.

51 All the metals combine with oxygen. Some, such as those of the alkalis and alkaline earths, unite with oxygen so readily that they have to be preserved out of contact with air. Other metals withstand the action of oxygen at the ordinary temperature, but combine with it when heated. When the metals are easily volatile, as is the case with magnesium and zinc, they burn with a bright flame in the air or in oxygen. If they do not volatilize readily, like tin and lead. the metals gradually undergo oxidation without evolution of light. A few metals such as gold and platinum cannot be made to unite directly with oxygen, even at the highest temperatures. The oxides of such metals can however be prepared by indirect means; chlorine attacks all metals and if the chlorides of these metals which are not directly oxidisable be decomposed by an alkali, their oxides or hydroxides are formed: thus—

$$2AuCl + 2KOH = Au_2O + 2KCl + H_2O.$$

Representatives of each of the three classes—basic oxides, peroxides, and acid-forming oxides—into which the oxides in general may be roughly divided (vol. i. p. 234) are found among the oxides of the metals.

1 *Basic Oxides.*—The term basic oxide is only applied to such oxides as react with acids to form the corresponding salt and water, and hence all these oxides are formulated as derived from water by the replacement of hydrogen by a metal or a radical containing a metal united with oxygen. Thus in uranium oxide, UO_3, which yields salts such as $UO_2(NO_3)_2$, the

[1] *See* Ostwald, *The Scientific Foundations of Analytical Chemistry* (Macmillan).

hydrogen of water is replaced by the radical UO_2, which is also present in the salts. When only a part of the hydrogen is replaced by a metal or radical, the resulting compound is termed a hydroxide, *e.g.*, $Ca(OH)_2$. The hydroxides were formerly called hydrates, as they were supposed to be compounds of the oxides with water.

Many of the metals form several basic oxides and corresponding series of salts in which they have a different equivalent, as shown in the following list:

Mercurous oxide	Hg_2O	Mercuric oxide	HgO
Ferrous oxide	FeO	Ferric oxide	Fe_2O_3
Ferrous hydroxide	$Fe(OH)_2$	Ferric hydrate	$Fe(OH)_3$

It must be remembered that only the empirical formula of most of the oxides and hydroxides is known, and that therefore no conclusions as to the valency of the metal can be drawn from these formulæ. Thus ferrous oxide may, for all we know, have the formula Fe_2O_2 and the constitution O = Fe—Fe = O.

The basic oxides are as a rule obtained by the direct oxidation of the metal, or by one of the following methods:

(1) The decomposition by heat of a salt of the metal and an acid of which the anhydride is volatile or yields volatile decomposition products:

$$PbCO_3 = PbO + CO_2.$$
$$ZnSO_4 = ZnO + SO_3.$$
$$4Al(NO_3)_3 = 2Al_2O_3 + 12NO_2 + 3O_2.$$

(2) The decomposition of the hydroxide by heat:

$$2Cr(OH)_3 = Cr_2O_3 + 3H_2O.$$

The basic hydroxides are usually prepared as follows:

(1) By the reaction of a soluble hydroxide on a salt of the metal

$$2NaHO + ZnSO_4 = Na_2SO_4 + Zn(OH)_2.$$

The oxide itself is however sometimes formed in this reaction instead of the hydroxide:

$$2NaOH + 2AgNO_3 = 2NaNO_3 + Ag_2O + H_2O.$$

(2) By the direct combination of the oxide with water:

$$CaO + H_2O = Ca(OH)_2.$$

The hydroxides of the alkali-metals are the most soluble. They are termed *alkalis*, and are distinguished by their caustic taste. The hydroxides of the metals of the alkaline earths are less soluble. Most of the other hydroxides and basic oxides are almost insoluble in water. Exceptions to this are seen in the case of thallous hydroxide, which is very soluble in water, as well as in the oxides of lead, silver, and magnesium, which dissolve very slightly.

2 *Acid-forming Oxides.*—The hydroxides corresponding with these oxides are the acids, but only comparatively few of these are known in the free state among the derivatives of the metals. Like the basic oxides they are formulated as derived from water by the complete or partial replacement of the hydrogen by a metal or radical. They are usually obtained by the addition of a stronger acid to a salt derived from the acid-forming oxide in question:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + 2CrO_3 + H_2O.$$

It is a general rule that the acid-forming oxides of a metal contain more oxygen than the basic oxides of the same metal. Thus Bi_2O_3 is a basic oxide, while Bi_2O_5 is a weak acid-forming oxide; again VO is a basic oxide, whilst V_2O_5 yields a strong acid which forms stable salts.

3 *Peroxides.* — The term peroxide is applied generally to oxides which are neither basic nor acid forming, but contain more oxygen than the basic oxides of the same metal. Many of these peroxides appear to be derived from hydrogen peroxide in the same way as the basic and acid-forming oxides are derived from water. Thus, when they are treated with an acid, they yield a salt and hydrogen peroxide:—

$$Ba\begin{matrix}O\\|\\O\end{matrix} + 2HCl = BaCl_2 + H.O.O.H.$$

while some of them may be prepared by double decomposition between a salt of the metal and hydrogen peroxide.

In some cases such oxides are to be considered as having a mixed constitution, part of their oxygen being derived from water and part from hydrogen peroxide.

Peroxides which are not true derivatives of hydrogen peroxide, on the other hand, act in the presence of acids simply as oxidising agents. Thus when they are treated with hydrochloric acid, chlorine is evolved and the salt corresponding to a lower basic oxide is formed:

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

It is however impossible to employ this reaction as the basis of a rigid classification of the peroxides, since the behaviour of the various oxides towards hydrochloric acid has not been sufficiently investigated.

This action of hydrochloric acid on the higher oxides of the metals is frequently employed for the determination of the composition of these oxides and for their analytical estimation (Bunsen). The chlorine evolved from a known weight of the oxide is collected in a solution of potassium iodide and estimated by means of a standard solution of sodium thiosulphate. Many oxides which are not peroxides undergo the same reaction, a salt corresponding with a lower oxide being formed:

$$2CrO_3 + 12HCl = 6H_2O + 2CrCl_3 + 3Cl_2.$$

4 In addition to the classes of oxides which have already been discussed, many metals also yield *sub-oxides*, which contain less oxygen than the lowest oxide of the metal which is capable of yielding salts, *e.g.*, Cu_4O, Pb_2O, &c. The constitution of these oxides is not at present understood. Many metals moreover form *intermediate oxides*, to which no corresponding salts are known. Such oxides are intermediate in composition between two of the other oxides of the metal, and generally yield a mixture of products when treated with acids. Thus magnetic oxide of iron, Fe_3O_4, which is intermediate between ferrous and ferric oxides, FeO and Fe_2O_3, yields a mixture of ferrous and ferric chlorides when it is dissolved in hydrochloric acid:

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O.$$

Red lead, Pb_3O_4, on the other hand, which is intermediate between the monoxide and the peroxide of lead, PbO and

PbO_2, is converted into lead nitrate and lead peroxide when it is treated with dilute nitric acid:

$$Pb_3O_4 + 2HNO_3 = Pb(NO_3)_2 + PbO_2 + H_2O.$$

52 It will be seen from the foregoing that the classification of the oxides is mainly based on the behaviour of these compounds with regard to the formation of salts. Since an oxide may exhibit varying behaviour in this respect when it is placed under different conditions, it follows that the same oxide may be found as a member of more than one class. Many oxides for example act as basic oxides towards strong acids, but as acid-forming oxides towards strong bases. Thus aluminium hydroxide is dissolved by sulphuric acid with formation of aluminium sulphate:

$$2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O,$$

and also by caustic soda with formation of sodium aluminate:

$$Al(OH)_3 + NaOH = Al(OH)_2ONa + H_2O.$$

Again when black oxide of manganese, MnO_2, is warmed with hydrochloric acid, chlorine is evolved and manganous chloride is formed, so that the oxide behaves as a peroxide:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

At a lower temperature however an unstable salt is formed which is only known in solution, so that in this case the oxide acts as a basic one:

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

The same oxide can also be made to combine with strongly basic oxides such as lime, CaO, to form a number of unstable salts, the calcium manganites, such as $CaO.MnO_2$, in which it plays the part of an acid-forming oxide.

53 Salts may be classed into several groups.

(1) *Normal salts* are those in which the whole of the replaceable hydrogen of an acid is completely replaced by a metal. These were formerly called *neutral salts*, or *salia media*, because it was noticed that when an alkali was added in the right

proportion to a powerful acid the resulting salt possessed neither an alkaline nor an acid reaction. This, however, as has already been explained (p. 88), is not the case with every normal salt.

Polybasic acids can form salts containing two or more different metals; thus, for instance, potassium sodium carbonate, $CO\begin{cases}OK\\ONa.\end{cases}$ Polyatomic metals, on the other hand, may give rise to salts which contain two acid radicals: thus, $Sr\begin{cases}ONO_2\\OC_2H_3O\end{cases}$, a compound which is at the same time a nitrate and an acetate; as another and more complex example the mineral vanadinite may be cited, $VO\begin{cases}O\\O\\OCaCl\end{cases}\begin{matrix}\\\\\end{matrix}Ca$, which is a calcium salt of tribasic vanadic acid and at the same time a chloride.

The salts which are formed by the union of an acid-forming oxide with a normal salt, or when an acid salt is heated so as to lose water, and which are sometimes called acid salts, are really to be considered as normal salts derived from complex acids, which, however, often do not exist in the free state. Sodium pyrophosphate, for instance, which is obtained by heating ordinary sodium phosphate to redness:

$$\begin{matrix}PO\begin{cases}(ONa)_2\\OH\end{cases}\\PO\begin{cases}OH\\(ONa)_2\end{cases}\end{matrix} = \begin{matrix}PO\begin{cases}(ONa)_2\\O\\(ONa)_2\end{cases}\end{matrix} + H_2O,$$

is the normal salt of pyrophosphoric acid, $H_4P_2O_7$, which can be prepared in the free state and also yields an acid salt, $Na_2H_2P_2O_7$. The acids corresponding with potassium bichromate, $K_2Cr_2O_7$. borax, $Na_2B_4O_7$, &c., on the other hand are not known. Further examples of this class of substances are potassium disulphate or pyrosulphate, obtained by heating potassium hydrogen sulphate:

$$\begin{matrix}SO_2\begin{cases}OK\\OH\end{cases}\\SO_2\begin{cases}OH\\OK\end{cases}\end{matrix} = \begin{matrix}SO_2\begin{cases}OK\\O\\OK\end{cases}\end{matrix} + H_2O,$$

sodium metabisulphite, $Na_2S_2O_5$, and many complex phosphates, borates, and silicates (vol. i., pp. 599, 655, 821).

(2) *Acid salts* are formed when only a portion of the replaceable hydrogen contained in a polybasic acid is substituted by a metal. The acid salts often possess an acid reaction, as is the case with acid potassium sulphate, $SO_2\begin{cases}OK,\\OH\end{cases}$ but as we have seen this reaction is dependent on the nature of the acid and the base.

(3) *Basic salts* stand in the same relation to the basic hydroxides as the acid salts to the acids. They may be regarded as formed from the basic hydroxides by the reaction of only a part of their hydroxyl groups with the hydrogen of an acid, *e.g.*, $Zn\begin{cases}OH\\Cl\end{cases}$.

Some of these salts do not contain a hydroxyl group, and these may be considered as the normal salts of complex basic radicals. Thus, basic bismuth chloride (bismuth oxychloride), BiOCl, may be looked upon as the chloride of a basic radical, BiO(OH), derived by loss of water from bismuth hydroxide, $Bi(OH)_3$, just as pyrophosphoric acid is derived from orthophosphoric acid.

Basic salts are sometimes formed by the combination of a normal salt with an hydroxide. Thus, if a solution of lead nitrate be boiled with lead hydroxide, a basic lead nitrate is formed:

$$Pb\begin{cases}ONO_2\\ONO_2\end{cases} + Pb\begin{cases}OH\\OH\end{cases} = 2\,Pb\begin{cases}OH\\ONO_2\end{cases}$$

In the same way basic zinc chloride, $Zn\begin{cases}Cl\\OH\end{cases}$, may be obtained.

Basic bismuth nitrate, on the other hand, is obtained by the action of water on the normal salt:

$$Bi\begin{cases}ONO_2\\ONO_2\\ONO_2\end{cases} + 2H_2O = Bi\begin{cases}OH\\OH\\ONO_2\end{cases} + 2NO_2OH.$$

Amongst other basic salts may be mentioned:

Malachite. $CO\begin{cases}OCuOH\\OCuOH\end{cases}$

Blue Carbonate of Copper. $CO\begin{cases}OCuOH\\O\end{cases}Cu\quad CO\begin{cases}O\\OCuOH\end{cases}$

White Lead. $CO\begin{cases}OPbOH\\O\end{cases}Pb\quad CO\begin{cases}O\\OPbOH.\end{cases}$

Basic Mercuric Sulphate.

$$SO_2\begin{Bmatrix} OHgO \\ OHgO \end{Bmatrix}Hg.$$

(4) *Double Salts.* The term double salt is applied somewhat loosely to salts formed by the combination of a molecule of one salt with one or more molecules of another salt or of an acid, &c. Thus the substances represented by the formulæ, $KF+HF$, $Al_2(SO_4)_3+K_2SO_4+24H_2O$, &c., are called double salts. Very little is known about the constitution of such substances since they are generally decomposed, at all events to some extent, when they are dissolved in water, although they separate out again unchanged when the solution is concentrated. In many cases they are undoubtedly salts of complex acids or bases.

Solubility of Salts.

54 A very important property of salts is the manner in which they behave when treated with water. Strictly speaking all salts are soluble to some extent under these circumstances, but in many cases the amount dissolved is so minute that for most purposes it may be neglected, and it is therefore usual to roughly classify salts as soluble, sparingly soluble, and insoluble in water.

The following table illustrates the variation in the solubility of different salts:

One Hundred Parts of Water dissolve at 15—18°.

	Parts.
Potassium carbonate, K_2CO_3	110·5
Calcium chloride, $CaCl_2$	66
Sodium chloride, NaCl	35·9
Potassium nitrate, KNO_3	26
Potassium sulphate, K_2SO_4	10·3
Potassium perchlorate, $KClO_4$	1·5
Calcium sulphate, $CaSO_4,2H_2O$	0·26
Strontium sulphate, $SrSO_4$	0·0107
Lead sulphate, $PbSO_4$	0·0046
Barium sulphate, $BaSO_4$	0·00026
Silver iodide, AgI	0·00001

When a salt is dissolved in water a reduction of temperature generally occurs, inasmuch as heat is absorbed by the passage of the solid to the liquid condition. Certain anhydrous salts, however, evolve heat on treatment with water, possibly owing to their combination with the latter to form hydrates, the heat of the formation of these being greater than that absorbed by the liquefaction of the salt.

In the case of every salt there is a maximum quantity which can be dissolved at any particular temperature, but this quantity varies if the temperature be altered, increasing in the great majority of cases with increase of temperature. In some cases such as that of potassium chloride, the solubility increases proportionally with the temperature, but generally it increases more rapidly than the latter. In such cases the solubility at any temperature may be ascertained by means of interpolation formulæ similar to those employed in the calculation of the solubility of the gases, the different constants being of course obtained by direct experiment. Thus, for potassium nitrate, at t°, where S represents the solubility at that temperature, we have

$$S = 13{\cdot}32 + 0{\cdot}5738t + 0{\cdot}017168t^2 + 0{\cdot}0000035977t^3.$$

A very convenient method of representing the solubility of salts is by plotting the results in a curve as shown in Fig. 3, the abscissae giving the temperatures and the ordinates the number of parts of salt which dissolve in 100 parts of water.

If the solubility of a salt increases proportionally with the temperature the curve of solubility becomes a straight line, as in the case of potassium chloride, but in most cases the curve ascends more rapidly as the temperature increases. In a few cases, such as calcium hydroxide and the calcium salts of certain organic acids, the solubility decreases with the rise in temperature.

Considerable light has been thrown during the past few years on the changes which take place in solution especially by the researches of Ostwald and his pupils,[1] who have succeeded in clearing up a number of points for which no explanation had hitherto been given The action of water on a salt, or, speaking generally, of a solvent on any crystalline substance, is in the first place to liberate those molecules with which it is in

[1] Published in the *Zeit. Phys. Chem.*, 1887—1896; see also Ostwald, *Lehrbuch der allgemeinen Chemie*, vol. i.

contact, and to allow them to distribute themselves equally throughout the liquid; this process then continues, provided an excess of the salt is present, until no further quantity of the latter is dissolved, a condition of equilibrium being thus estab-

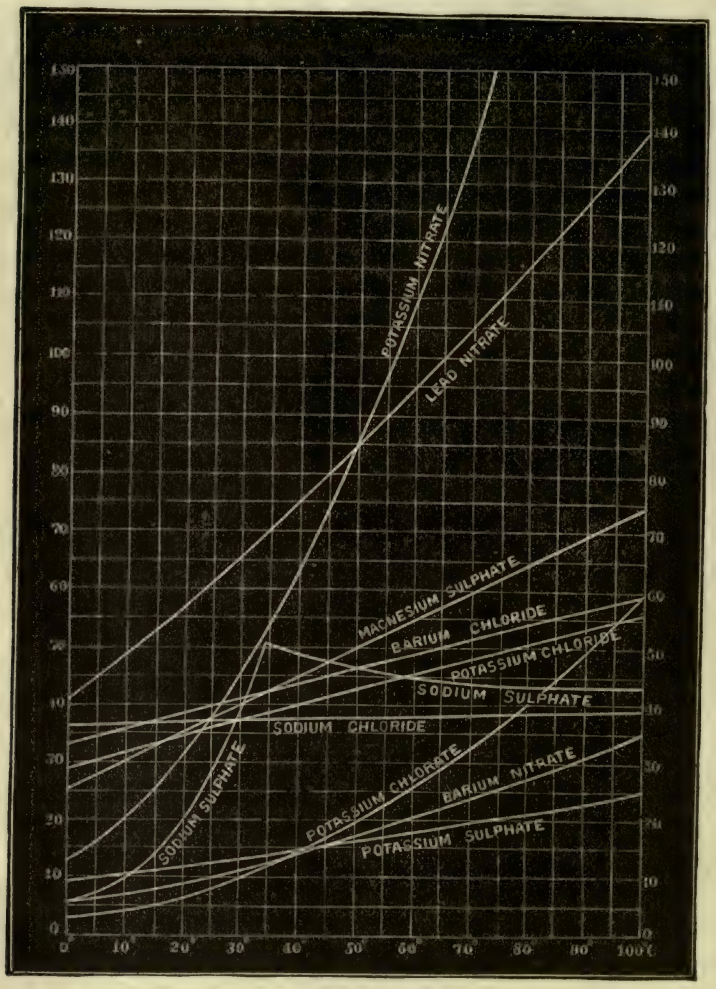


FIG. 3.

lished between the solution and the salt. As already shown, this point varies according to the nature of the salt and the temperature. Hence it follows that the maximum solubility depends upon the exact nature of the solid present, and there-

fore when a salt crystallises in two different forms the solubility may be different in the two cases. Again, the solubility of an anhydrous salt is also different from that of its hydrates, as for example in the case of calcium sulphate, which is much more soluble in the anhydrous state than when combined with two molecules of water to form gypsum, and this fact is of great practical importance, inasmuch as it is the cause of the setting of plaster of Paris (*q.v.*).

The recognition of the fact that the solubility depends on the exact nature of the salt has also supplied the explanation of certain cases of abnormal solubility, of which sodium sulphate is a typical example. As will be seen from the diagram, Fig. 3. the solubility of this salt rises rapidly from 0—33°, but from that point decreases and is considerably less at 100° than at 33°, It was formerly supposed that up to 33° the liquid contained the hydrate $Na_2SO_4 + 10H_2O$ in solution, and that above this temperature the latter underwent dissociation, the solution then containing the anhydrous salt. There is, however, no evidence of any sudden change in the properties of the solution, such as its vapour pressure or viscosity, at any point, and it has been shown that the above behaviour is really due, not to any change in the solution, but to a change in the solid substance with which it is in equilibrium. Up to 33° the solid salt present is $Na_2SO_4 + 10H_2O$, and below that temperature the curve represents the solubility of this hydrate in water; at 33° the crystals of the hydrate are dissociated into water and the anhydrous salt, and above that temperature the curve represents the solubility of the latter in water, which decreases with increase of temperature; the curve, therefore, is a combination of two separate solubility curves which meet at 33°. When a solution which has been saturated at 33° is warmed, the anhydrous salt is deposited, whilst when it is cooled the hydrate $Na_2SO_4 + 10H_2O$ separates out.

55 *Supersaturated Solutions.*—When a solution of a salt free from any undissolved crystals is allowed to cool quietly in closed vessels, it is frequently observed that no crystals separate out, although the quantity of salt contained in the solution is greater than that which can under ordinary conditions be dissolved at that temperature; such solutions are termed *supersaturated*. This is very readily shown in the case of many salts containing water of crystallisation, such as sodium sulphate, thiosulphate, and acetate. If, however, a crystal of

the salt be added a rapid crystallisation occurs, and the clear solution is then found to contain the normal amount of dissolved salt. Sodium acetate is a salt which is well adapted to show the phenomenon of supersaturation in a striking manner. For this purpose the crystallised salt is gently warmed in a flask with one quarter of its weight of water until all is dissolved, the liquid filtered if it is not perfectly free from suspended matter, and placed in a flask, the neck of which is closed with a plug of cotton-wool. If the smallest crystal of sodium acetate be thrown into the liquid when cold, crystallisation at once commences round the small particle, and in a few seconds the whole has assumed the solid form, the change being accompanied by a considerable rise of temperature. This singular crystallisation appears to be brought about only when the solution comes in contact with a crystal of the identical salt which separates out, or of one which is isomorphous with it, or when the solution is cooled to a sufficiently low temperature, which varies according to the nature of the salt. Thus if a supersaturated solution of sodium acetate, prepared as just described, be poured gently on to the surface of a supersaturated solution of sodium thiosulphate made by simply melting the crystals of the hydrated salt in a long test-tube, and the whole allowed to cool, it is found that when a crystal of sodium thiosulphate is dropped into the tube it falls through the lighter solution of sodium acetate without inducing crystallisation, but causes the immediate formation of crystals as soon as it comes into the heavier solution of sodium thiosulphate. A supersaturated solution of magnesium sulphate may be made to crystallise by adding either magnesium sulphate itself or any one of the isomorphous sulphates of iron, zinc, nickel, &c., whilst sodium sulphate, sodium chloride, &c., have no action upon it. Supersaturated solutions of sodium sulphate crystallise very readily when exposed to the air, and it has been shown that this is due to the presence of minute crystals of this salt in the atmosphere. The whole phenomenon is very similar to that of superfusion, and like the latter, it has not yet been completely investigated.

Metallic salts are, as a rule, insoluble or very sparingly soluble in organic liquids. Some liquids, however, such as alcohol, acetic acid, ether, &c., dissolve certain salts with some freedom. Thus calcium chloride, calcium nitrate, potassium iodide, and many others are soluble in alcohol, whilst mercuric chloride and

zinc chloride are soluble both in alcohol and ether, and the solubility of cadmium bromide in a mixture of these two solvents is made use of in the wet processes of photography. Salts which are insoluble in alcohol are precipitated in the form of minute crystals when alcohol is added to their aqueous solutions, and this substance is therefore often used in quantitative analysis, having been first proposed for this purpose by Bergman in 1778.

Fusibility and Volatility of Salts.

56 Most of the metallic salts melt at temperatures beyond the range of the ordinary mercurial thermometer, and the melting point has only been determined with accuracy in comparatively few instances. As already mentioned (p. 57) Carnelley has shown that in the case of the salts which the metals form with the same acid, the melting point is a periodic function of the atomic weight of the metal contained in the salt, just as is the case with the metals themselves.

The boiling point has only been determined in the case of a few of the haloid salts, but the comparative volatility of certain salts has been approximately ascertained by Bunsen[1] by the following method: A small bead of each salt weighing one centigram is placed in the zone of fusion of a Bunsen flame, having a temperature of about 2300°, and the time ascertained which the bead takes to volatilise. The following numbers give the relative volatility for certain salts, that of sodium chloride being taken as the standard:

	NaCl	KCl	KBr	KI	K_2SO_4	K_2CO_3
Seconds.	84·2	63·4	41·0	29·8	665·2	272·0
Volatility.	1·000	1·288	2·055	2·828	0·127	0·310

It has also been recently shown by Bailey[2] that certain salts are slightly volatile when their aqueous solutions are evaporated, even when all precautions are taken to prevent their being carried over mechanically. This phenomenon has been more closely examined in the case of the chlorides of the alkali metals, and it has been shown that the volatility increases with the

[1] *Phil. Mag.* 1866, (4) **32**, 85.
[2] *Journ. Chem. Soc.* 1894, i. 445.

molecular weight of the chloride and the concentration of the solution.

Generic Properties of Salts.

57 The generic properties of the metallic salts have in most cases been already given in Vol. I., under the respective acids. The most important points may, however, be shortly recapitulated here.

Fluorides.—In their general properties the fluorides closely resemble the chlorides, but are, as a rule, much less soluble in water. Potassium, ammonium, silver, and stannous fluoride dissolve readily, the sodium and lithium salts less easily, those of the alkaline earth metals very sparingly in water, and the remainder are almost insoluble. The alkali fluorides unite with hydrogen fluoride and with the fluorides of the more electro-negative elements to form double fluorides which usually crystallise well. Thus we have :—

Potassium hydrofluoride, $KF,HF = KHF_2$
Potassium borofluoride, $KF,BF_3 = KBF_4$
Potassium silicofluoride, $2KF,SiF_4 = K_2SiF_6$
Potassium tantalofluoride, $2KF,TaF_5 = K_2TaF_7$

Chlorides.—The greater number of the chlorides are solid bodies, but a few, such as stannic chloride, $SnCl_4$, titanic chloride, $TiCl_4$, and antimony pentachloride, $SbCl_5$, are liquids, and these as well as mercuric chloride, $HgCl_2$, and antimony trichloride, $SbCl_3$, may be readily volatilised. The majority melt at a fairly high temperature, and can only be volatilised at a red heat or higher temperature, and some few, such as gold chloride, $AuCl_3$, and platinum chloride, $PtCl_4$, decompose into their elements when strongly heated. With the following exceptions they dissolve readily in water: silver chloride, AgCl, mercurous chloride, HgCl, cuprous chloride, Cu_2Cl_2, platinous chloride, $PtCl_2$, palladious chloride, $PdCl_2$, thallous chloride, TlCl, and lead chloride, $PbCl_2$; the last two dissolve to a slight extent in cold, and readily in hot water.

In some cases the chlorides are chemically acted on by water, giving rise to basic compounds; thus bismuth and antimony trichloride yield an insoluble oxychloride,

$$BiCl_3 + H_2O = BiOCl + 2HCl$$

others, such as titanium chloride, are completely decomposed into hydrochloric acid and a hydroxide of the metal.

Many double chlorides are also known similar to the double fluorides, but the tendency to the formation of these is not so great as in the former case. The most characteristic are the *platinochlorides*, such as potassium and ammonium platinochlorides, K_2PtCl_6 and $(NH_4)_2PtCl_6$, which may also be looked upon as salts of the acid, H_2PtCl_6. The chlorides are distinguished from the bromides and iodides by the fact that when heated with sulphuric acid and potassium bichromate they yield chromyl chloride, CrO_2Cl_2, which is a dark red liquid, and is converted by water into chromic and hydrochloric acids. The bromides and iodides on similar treatment yield bromine and iodine respectively.

Bromides.—The metallic bromides resemble most closely the corresponding chlorides. Silver bromide is, however, less soluble in ammonia than silver chloride. The bromides when treated with concentrated sulphuric acid are decomposed with evolution of hydrobromic acid, free bromine, and sulphur dioxide. Free chlorine liberates bromine from a solution of a bromide.

Iodides.—This group of salts possesses great analogy with the corresponding chlorides and bromides. It is distinguished from them by the fact that silver iodide is insoluble in ammonia, and that concentrated sulphuric acid decomposes the iodides with liberation of iodine and sulphur dioxide. Mercuric iodide is an insoluble scarlet powder, whilst lead iodide forms a yellow precipitate. This latter dissolves in large quantities of boiling water, and is again deposited on cooling in bright golden flakes. The soluble iodides are decomposed by chlorine, bromine, and nitrous acid, with liberation of iodine.

Cyanides.—These salts are classed with the haloid salts, which they closely resemble in properties. The cyanides of the alkali and alkaline earth metals and mercury are soluble in water; the remainder are insoluble but dissolve in a solution of potassium cyanide, forming double cyanides. Two different classes of the latter exist, viz.:—

(1) Those which still retain the characteristic properties of a cyanide, and in which both metals can be detected by the usual tests, as for example, potassium silver cyanide, KCN, AgCN, obtained by the action of potassium cyanide on silver cyanide.

(2) Those in which the metal forming the insoluble cyanide no longer shows the usual reactions, and in which also the properties of a cyanide cannot be observed, such as potassium ferrocyanide.

According to the theory of the dissociation into ions, the difference in these two series of salts is explained in the following manner. In the first series, the double salt on solution in water is partly dissociated into three different kinds of ions, namely the two metallic ions and the cyanogen ion; thus potassium silver cyanide solution contains potassium, silver, and cyanogen ions, and therefore gives the usual reactions of these ions. In potassium ferrocyanide, on the other hand, dissociation takes place into only two different ions, namely, potassium and ferrocyanogen, $Fe(CN)_6$; the solution gives, therefore, the reactions of potassium, but instead of those of ionic iron and cyanogen, reactions which are due to the new negative ion, $Fe(CN)_6$.

Hypochlorites.—The salts of hypochlorous acid are almost unknown in the free state, as they are generally obtained together with chlorides by the action of chlorine on cold solutions of the hydroxides of the metals, and cannot be isolated from the solution. The solutions bleach organic colouring matters slowly, but on addition of hydrochloric acid the bleaching is quickly effected, chlorine being evolved thus:—

$$NaCl + NaClO + 2HCl = Cl_2 + 2NaCl + H_2O.$$

Chlorates.—The chlorates are all soluble in water, that of potassium being one of the least soluble, and they all decompose on heating, giving off oxygen and leaving the chloride. When a solid chlorate is acted on by strong sulphuric acid a yellow explosive gas, ClO_2, is evolved, the odour of which at the same time resembles that of chlorine and that of burnt sugar.

Perchlorates.—These salts are also, without exception, soluble in water, the least soluble being the potassium salt. On addition of sulphuric acid they do not evolve an explosive gas, but are converted into perchloric acid; like the salts of the other oxy-acids of chlorine they are completely decomposed by heat into oxygen and the chloride of the metal.

Iodates and Periodates.—Several series of both iodates and periodates are known, which have already been described (vol. i., pp. 332–336).

Sulphides.—The compounds of the metals with sulphur correspond in general with the oxides, although there are cases in which no sulphide is known corresponding to a particular oxide, and *vice versa.* The sulphides and hydrosulphides of the alkali metals, and the hydrosulphides of metals of the alkaline earths are soluble in water; the solutions when allowed to remain in contact with free sulphur are converted into polysulphides, and are oxidised by the oxygen of the air to sulphites, thiosulphates, and sulphates. The remaining sulphides are almost all insoluble in water, some of them being dissolved by dilute acids with evolution of sulphuretted hydrogen, whilst others undergo no change under these conditions. The different solubilities of the sulphides in water and acids are taken advantage of in the qualitative and quantitative separation of the metals.

The sulphides of the more electro-negative metals dissolve in solutions of the alkaline sulphides, forming sulpho-salts just as the corresponding oxides unite together to form oxy-salts. Thus potassium oxide combines with arsenic oxide to form potassium arsenate, and potassium sulphide combines with arsenic sulphide to form potassium thioarsenate.

$$3K_2O + As_2O_5 = 2K_3AsO_4$$
$$3K_2S + As_2S_5 = 2K_3AsS_4$$

Subjoined is a list of some of the analogous oxy-salts and sulpho-salts which have been prepared, in the formulæ of which M represents an atom of a monad metal.

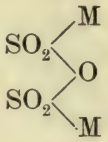
Oxy-salts.	Sulpho-salts.
Carbonates, M_2CO_3	Thiocarbonates, M_2CS_3
Pyrophosphates, $M_4P_2O_7$	Pyrothiophosphates, $M_4P_2S_7$
Metarsenates, $MAsO_3$	Metathioarsenates, $MAsS_3$
Ortharsenates, M_3AsO_4	Orthothioarsenates, M_3AsS_4
Metastannates, M_2SnO_3	Metathiostannates, M_3SnS_3
Orthostannates, M_4SnO_4	Orthothiostannates, M_4SnS_4

Similar salts are also known containing selenium and tellurium in place of sulphur.

Sulphites.—Sulphurous acid being a dibasic acid forms two series of salts, viz.: normal and acid sulphites, such as Na_2SO_3 and $NaHSO_3$. Those of the alkali metals are soluble in water, but the remainder are for the most part sparingly soluble or

insoluble, although they dissolve in a solution of sulphurous acid. They are fairly stable in the dry state but gradually oxidise in presence of moisture, forming sulphates. They are decomposed by dilute acids with evolution of sulphur dioxide, and if a reducing agent such as zinc be added, sulphuretted hydrogen is evolved, by which means small quantities of a sulphite may be readily detected. Oxidising agents such as chlorine, bromine, nitric acid, and potassium permanganate, convert sulphites into the corresponding sulphates.

In addition to these, a series of sulphites known as the *metabisulphites* or *disulphites* has been prepared, the constitution of which is probably represented by the general formula :—



Sulphates.—With the exception of those of barium, strontium, and lead, which are almost insoluble in water, and those of calcium, silver, and mercury, which are sparingly soluble, all the sulphates dissolve readily and separate on evaporating the solution in well-developed crystals usually containing a varying number of molecules of water of crystallisation. The metals of the alkalis form normal and acid sulphates, the metals of the alkaline earths and magnesium yield only normal sulphates, whilst many other metals form soluble normal salts as well as more or less insoluble basic sulphates. Many sulphates possess the property of forming crystallisable double salts. This is especially the case with the sulphates of the isomorphous metals of the magnesium group, which yield compounds with the sulphates of the alkali metals having the general formula $\overset{ii}{M}SO_4 + \overset{i}{M}_2SO_4 + 6H_2O$.

$MgSO_4 + K_2SO_4 + 6H_2O$
$CdSO_4 + (NH_4)_2SO_4 + 6H_2O$
$CuSO_4 + K_2SO_4 + 6H_2O$
$FeSO_4 + (NH_4)_2SO_4 + 6H_2O$

Another important group of the double sulphates is that of the *alums*, which have the general formula $\overset{iii}{M}_2(SO_4)_3 + \overset{i}{M}_2SO_4 + 24H_2O$

$$\begin{aligned}
&Al_2(SO_4)_3 + K_2SO_4 &&+ 24H_2O\\
&Fe_2(SO_4)_3 + (NH_4)_2SO_4 &&+ 24H_2O\\
&Cr_2(SO_4)_3 + K_2SO_4 &&+ 24H_2O\\
&Al_2(SO_4)_3 + Na_2SO_4 &&+ 24H_2O\\
&Al_2(SO_4)_3 + Ag_2SO_4 &&+ 24H_2O\\
&In_2(SO_4)_3 + (NH_4)_2SO_4 &&+ 24H_2O
\end{aligned}$$

Nitrides—Some of the metals, such as magnesium, vanadium, titanium, and lithium, unite with nitrogen when strongly heated in the gas, forming stable nitrides, but in most cases these compounds can only be obtained indirectly by the action of ammonia on their heated oxides or chlorides. They are usually dull brown or black powders, the composition of which has in many cases not been accurately determined, and a number of these are undoubtedly mixtures.

The salts of azoimide (vol. i., p. 472) form a special class of nitrides which contain the group $.N<\begin{matrix}N\\ \|\\ N\end{matrix}$; these are all extremely explosive substances.

Nitrites.—These salts are for the most part soluble in water, and are decomposed when strongly heated into oxides of nitrogen and the oxide of the metal. In solution they are oxidised by the oxygen of the air to nitrates.

Nitrates.—With the exception of one or two basic nitrates such as that of bismuth, all the nitrates dissolve in water, and usually crystallise well. They melt at low temperatures, and on further heating, those of the alkali and alkaline earth metals are converted, first into nitrites with evolution of oxygen, and then further decompose into oxides of nitrogen and the oxide of the metal; with the nitrates of the other metals the intermediate formation of nitrite is usually not observed, and in cases where the oxide is unstable at high temperatures the metal itself remains as the final product. Owing to the ease with which they lose oxygen the nitrates are frequently employed as oxidising agents.

Phosphides.—Most of the metals combine with phosphorus to form phosphides. Some of these, as, for example, the phosphides of iron and zinc, are crystalline, but a large number have only been obtained as difficultly fusible masses, which have not as yet been closely examined, and are probably far from pure. Those of the alkali and alkaline earth metals are decom-

posed by water with formation of gaseous or liquid hydrogen phosphide.

Hypophosphites, Phosphites, Phosphates, Arsenites, and Arsenates.—The relations between the different modifications of these acids, and the general properties of their salts have already been fully described (vol. i., pp. 582–601, 625–629).

Carbides.—Most of the metals combine with carbon when either they or their oxides are heated together with carbon to a very high temperature in an electric furnace. Those of the alkali and alkaline earth metals are dark-coloured substances, which are decomposed by water with formation of the hydroxide and evolution of acetylene, whilst that of aluminium yields methane in place of acetylene. Many of the other carbides crystallise well, and of these by far the most important are those of iron, which are always present in commercial iron and exert an immense influence on its properties.

Carbonates.—Most of the metals form salts with carbonic acid, the monovalent alkali metals yielding normal and acid salts of the general formulæ, M_2CO_3 and $MHCO_3$; a few metals, such as aluminium and chromium, do not appear to form carbonates, and others, such as magnesium, bismuth, and copper, yield basic carbonates.

With the exception of the carbonates of the alkali metals and of thallium all the carbonates are insoluble in water, but many of them dissolve in water containing carbonic acid, probably owing to the formation of an unstable acid carbonate. They are decomposed by heat with evolution of carbon dioxide, and formation of the oxide of the metal unless this is itself decomposed at the temperature employed, but the temperature at which the decomposition takes place varies considerably; thus the carbonates of the alkali metals are only slightly decomposed at a bright red heat, whilst those of the alkaline earth metals are completely decomposed at this temperature if the carbon dioxide is removed as it is formed, and the remainder decompose for the most part at a lower temperature.

The carbonates are decomposed by almost all acids with evolution of carbon dioxide and formation of the corresponding salt of the acid used, and this reaction frequently forms a very convenient method of preparation for the salts of any acid.

Borates and Silicates.—These salts have already been discussed in vol. i., pp. 650–656, 814–823.

CHEMICAL CHANGE.

58 The older chemists thought that substances only combined with one another when they possessed a common principle, and hence they gave the name of affinity (*affinis*, related) to the particular property in virtue of which substances unite. It was afterwards seen that substances which have nothing in common nevertheless react with one another chemically, and this was ascribed to a mutual attraction between the particles of the substances (Newton). It was, moreover, thought that this attraction was elective in its character, so that when the particles of three substances were all brought together, those two would combine between which there was the stronger attraction, to the exclusion of the third. Thus, if a substance A, capable of uniting with C, were presented to a compound BC, made up of two substances united together, no change would occur if the attraction of C for B were stronger than that of C for A; whilst if the opposite were the case, C would unite with A and leave B in the free state. This view was especially supported by Geoffroy (1718) and Bergman (1775), who drew up tables of affinity or attraction showing the order of the strengths of the affinities of the various bases, metals, &c., for the acids and other substances with which they were capable of combining. The true state of affairs was, however, first recognised by Berthollet, who demonstrated by a series of experiments that the course of a reaction does not depend solely on the affinities of the substances concerned, but also on the relative quantities of them which are present. Thus, according to the view held by Berthollet, it follows that "in opposing the body A to the combination BC, the combination AC can never take place; but that the body C will be divided between the bodies A and B proportionally to the affinity and the quantity of each."[1] These views were afterwards developed by Berthollet in his celebrated *Essai de Statique Chimique*.

The further progress of investigation in this department of chemistry[2] has confirmed the opinions expressed by Berthollet.

[1] *Researches into the Laws of Chemical Affinity*, p. 6 (English Translation, London, 1804).

[2] A fuller account of this subject will be found in Lothar Meyer, *Modern Theories of Chemistry*; Nernst, *Theoretical Chemistry*; Ostwald, *Allgemeine Chemie*, vol. ii.

When careful experiments are made it is found that very frequently the whole of the substances concerned in a reaction or decomposition do not undergo the change, but that a certain fraction of the original substances remains unaltered, and that those cases in which a complete reaction appears to occur are in reality cases in which equilibrium is only established when an exceedingly small proportion of the substances originally concerned is left unchanged.

Thus, when calcium carbonate is heated in a closed vessel it evolves carbon dioxide until a certain pressure of this gas is reached, after which no further change in composition occurs until the conditions are in some way altered. If the temperature be increased more carbon dioxide is evolved, until another definite pressure, higher than the previous one, is attained, after which the mass again undergoes no further change so long as the circumstances remain unaltered. It is, moreover, found that to every temperature there is a corresponding pressure of carbon dioxide, which is perfectly definite and constant, and which increases as the temperature rises, as may be seen from the table given.[1]

Temperature.	Pressure.
547°	27 mm. of mercury.
610	46 „ „
740	255 „ „
810	678 „ „
865	1333 „ „

If, on the other hand, the temperature be kept constant, but the pressure of the carbon dioxide lowered by pumping out some of the gas, an additional quantity of the calcium carbonate decomposes until the original pressure is again attained. In order to completely decompose calcium carbonate by heat it is therefore necessary to keep the pressure of the carbon dioxide as low as possible, and it is only when this it done that complete decomposition can be effected. This is brought about by heating the carbonate in a current of air freed from carbon dioxide, or more usually in the open air, in which the pressure of carbon dioxide is so small that it may be neglected, and hence it is that in the ordinary form of the experiment the decomposition is practically complete.

[1] Chatelier, *Compt. Rend.* 1886, **102**, 1243.

Reactions then, as a rule, are not complete, but only proceed until a certain definite state of equilibrium is set up. This state of equilibrium is quite analogous to what occurs in many physical phenomena. Thus, when water or any liquid evaporates in a confined space, the evaporation only proceeds until the vapour of the liquid exerts a certain definite pressure on the surface of the liquid; this pressure is likewise constant for any particular temperature and increases rapidly as the temperature rises. As soon as it has been attained a condition of equilibrium is set up, and the relative amounts of vapour and liquid then remain unaltered so long as the other conditions remain the same. The maintenance of this state of equilibrium depends upon the fact that the evaporation of the liquid is proceeding at exactly the same rate as the condensation of the vapour, so that the actual proportion of vapour to liquid remains the same, whilst individual particles of the liquid are continually escaping from its surface, and as many others returning to it from the vapour above.

Precisely the same considerations hold with regard to chemical equilibrium. Thus, recurring to the example of calcium carbonate, when equilibrium is set up at any particular temperature, we may suppose that the calcium carbonate is being decomposed into lime and carbon dioxide at exactly the same rate as the last two are recombining to form calcium carbonate.

All cases of simple chemical equilibrium may be considered from the same standpoint as being brought about by two reactions proceeding in opposite senses and at equal rates, so that the actual proportions of the substances present undergo no change. Reactions of this kind, which can proceed in either sense according to the circumstances of the experiment, are known as reversible reactions, and are often indicated symbolically by two arrows pointing in opposite directions placed between the two parts of the equation

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

It appears probable that all chemical changes really belong to the class of reversible reactions, although the conditions under which the reversal of the change can be brought about have in many cases not yet been determined.

Velocity of Reactions.

59 *Conditions of Chemical Equilibrium.*—We have seen that the condition of equilibrium depends on the velocity of the reactions to which the equilibrium is due, and it is therefore of great importance to ascertain on what conditions the velocity of a reaction depends. Whenever chemical action is set up, a definite period elapses bfeore equilibrium is attained, and the change ceases. In many cases, however, the reaction proceeds so rapidly that this time cannot be measured; thus when hydrochloric acidis added to caustic soda solution, when silver nitrate is added to solution of sodium chloride, and in many similar instances, the reaction appears to be complete as soon as the substances have been mixed together and thus brought into contact, and no measurement of the rate of the reaction is possible. When, however, the reaction proceeds slowly, such measurements can be made, and it is thus possible to ascertain the influence of various circumstances on the velocity with which the change is effected. The most important result of the experiments which have been made on this subject is the generalization known as the law of the action of mass, which states that the velocity of any reaction is directly proportional to the amounts of the active substances present. This law follows from the investigations of Wilhelmy (1850), Harcourt and Esson (1866), Guldberg and Waage (1867), van't Hoff and others. The experiments of Harcourt and Esson[1] may be cited as an instance of the actual results obtained. They were carried out by allowing potassium permanganate to act on oxalic acid dissolved in water in presence of manganese sulphate, which is necessary to the reaction, and sulphuric acid. The amounts of the various substances present could all be varied, and the reaction was very thoroughly investigated. The amount of unaltered potassium permanganate present in the solution at any moment was determined by adding an excess of potassium iodide solution and estimating the iodine liberated.

The simplest case of this reaction occurs when the oxalic acid is in large excess, as under these circumstances the change in the amount of this substance may be neglected. It was accordingly found that under these conditions the rate at

[1] *Phil. Trans.* 1866, 193.

which the potassium permanganate disappears is at any moment proportional to the amount of it which is still left unreduced in the solution. This may be expressed more simply by saying that the same fraction of the permanganate actually present in the solution is reduced in each successive interval of time. In the following table the results obtained with a mixture of the molecular composition $2KMnO_4 + 14MnSO_4 + 108C_2H_2O_4$ are compared with those calculated on the assumption that the law of the action of mass really holds for this particular change, and, as will be seen, the agreement is excellent:

Time.	Amount of Permanganate left in the solution.	
	Observed.	Calculated.
2	94·8	94·8
5	87·9	87·6
11	74·9	74·7
27	49·3	48·9
35	39·1	39·6
47	28·3	28·8
68	17·0	16·5

In reactions in which the amounts of two substances are both altering at the same time, such as the decomposition of ethyl acetate by caustic soda,

$$C_2H_3O_2C_2H_5 + NaOH = C_2H_5OH + NaC_2H_3O_2,$$

the matter is more complicated, since the rate of the reaction at any moment is now proportional to the product of the active masses of the two substances present at that moment. Here again, however, the observed numbers agree well with those which are obtained by calculation from the law of the action of mass. In many cases, especially when solutions of weak acids or bases are concerned, the active mass is not identical with the actual mass of the substance present, since in such reactions only that portion of the substance which is electrolytically dissociated is active in producing the change. Thus, when an equivalent amount of ammonia, which is dis-

sociated to a much smaller extent than caustic soda, is substituted for the latter in the above reaction, the rate becomes much slower, and is still further diminished by the addition of any substance, such as an ammonium salt, which diminishes the dissociation of the ammonia.

The rate at which a chemical reaction proceeds is often enormously increased by rise of temperature, this being particularly well seen in the case of many gases. At the ordinary temperature hydrogen and oxygen are only in equilibrium when they are almost completely united to form water, but the two gases react so slowly that even when preserved for years it is impossible to observe the formation of an appreciable amount of water. When the temperature is raised, however, the reaction takes place so rapidly that explosion occurs, and when the mass has cooled to the original temperature again it is found that the gases are now in their proper state of equilibrium.

60 *Chemical Equilibrium.*—Most of the reactions hitherto considered have been chosen from amongst those in which equilibrium does not occur until practically the whole of the substances originally present have undergone the change. When this is not the case, however, but equilibrium is reached while there is still an appreciable amount of the original substance or substances remaining, it must be remembered that there are two reactions proceeding at the same time. If p and q represent the active masses of the two original substances A and B which are reacting according to the equation

$$A + B \rightleftarrows C + D,$$

then the velocity v of the reaction between them is, according to the law of the action of mass,

$$v = kpq,$$

where k is a constant, the value of which depends on the nature of the substances, the temperature, &c. Similarly if p' and q' be the active masses of the products of the reaction, C and D, the velocity of the reverse reaction between these, which results in the reproduction of the substances A and B, is

$$v' = k'p'q'.$$

The velocity of the resultant reaction, which can be measured by experiment, will then be

$$v - v' = kpq - k'p'q',$$

and when this is equal to zero, *i.e.*, when the two reactions proceed at equal rates, the system is in equilibrium, in which condition, therefore, we have the equation

$$kpq = k'p'q', \text{ or } \mathrm{K} = \frac{k}{k'} = \frac{p'q'}{pq}.$$

The ratio $\frac{k}{k'} = \mathrm{K}$ is known as the *constant of equilibrium*, and can be determined experimentally by ascertaining the amounts of the various substances which are actually present when equilibrium is established. Thus when alcohol is mixed with a molecular proportion of acetic acid at the ordinary temperature the following reaction occurs:

$$\mathrm{C_2H_5OH} + \mathrm{C_2H_4O_2} \rightleftarrows \mathrm{C_2H_5OC_2H_3O} + \mathrm{H_2O}.$$

The amount of change which has occurred during any period can readily be measured by simply titrating the acid still present and subtracting the amount thus found from that originally taken. The quantities of alcohol, ethyl acetate and water present can then all be calculated from this number by means of the equation representing the reaction. When equilibrium is established, a process which requires several days at the ordinary temperature, it is found that $\frac{2}{3}$ of the alcohol and acetic acid have undergone the reaction, whilst $\frac{1}{3}$ of each is left unaltered. Exactly the same state of equilibrium is reached if equivalent amounts of ethyl acetate and water are taken and allowed to react. In this condition therefore, $pq = \frac{1}{3} \times \frac{1}{3} = \frac{1}{9}$, whilst $p'q' = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9}$, so that

$$\mathrm{K} = \frac{p'q'}{pq} = 4.$$

When the value of the equilibrium constant has once been determined, it is possible to calculate the state of equilibrium when the substances are mixed in any proportions. Thus if A be the number of molecules of alcohol and B of acetic acid in the above instance, and if x be the number of molecules of

acid which react with the alcohol, then in the condition of equilibrium

$$p = \mathrm{A} - x,\ q = \mathrm{B} - x,\ p' = q' = x.$$

By substituting these values in the equation given above, the value of x can be obtained. The numbers calculated in this way agree well with those obtained by experiment.

It is found experimentally that if a large excess of alcohol be taken, practically the whole of the acetic acid is converted into ethyl acetate, whilst if a large excess of acid be taken, almost the whole of the alcohol undergoes the reaction. These facts have an important bearing upon the reactions used in analytical processes. In these cases it is essential that equilibrium be not established until practically the whole of the substance which is being estimated has undergone the particular reaction. In the processes of gravimetric analysis the substance which is being analysed, or some one of its elements, is converted into a sparingly soluble compound. In this way the product which is precipitated is continually withdrawn from the solution, the equilibrium is thereby disturbed and fresh quantities of the substance are formed and precipitated, the reaction thus proceeding until it is practically complete. This effect is further aided in most cases by the use of an excess of the reagent, which, as we have just seen, tends to increase the amount of the other substance which undergoes the reaction. In the processes of volumetric analysis it is also necessary to choose reactions for which the constant of equilibrium is very high, and which moreover proceed rapidly. Thus the reaction between equivalent quantities of caustic soda and hydrochloric acid can be utilised for estimating the amount of the former present, because the reaction proceeds rapidly, and equilibrium is only established when practically the whole of the acid and alkali present have reacted. The completion of the reaction is therefore indicated by the fact that the solution becomes neutral. On the other hand, it is impossible to estimate alcohol by titration with hydrochloric acid, because the constant of equilibrium for this reaction is low (8·44 at 99°[1]), and equilibrium is attained long before the whole of the alcohol has been converted into ethyl chloride, and therefore before the solution becomes neutral, so that it is

[1] Cain, *Zeit. Phys. Chem.* (1893), **12**, 751.

impossible to ascertain by the aid of an indicator when an equivalent of the acid has been added.

Among the many instances of chemical equilibrium which have been experimentally studied, the only one which can be mentioned here in addition to those already discussed, is the phenomenon of the dissociation of gases. When a gas is decomposed by heat into several new molecules, which may either be all of the same kind as in the case of nitrogen peroxide, N_2O_4, or of different kinds as in the case of phosphorus pentachloride, and these reunite to form the original gas when the whole is allowed to cool, the gas is said to dissociate when heated. In such a case the quantities of the several gases present are proportional to the pressure which they exert in the mixture. Thus if p be the pressure due to the undissociated molecules, and p_1 that of each of the two new gases formed, the equation of equilibrium becomes

$$K = \frac{p_1^2}{p}$$

If now the pressure of one of the products of dissociation be increased by adding some of it to the mixture without allowing the volume of the whole to increase, it follows that the numerator of this fraction must increase, and that therefore, since K is constant, p must also increase. In other words the dissociation of the gas must be diminished. This result has been experimentally verified in many cases. Thus when phosphorus pentachloride is vaporised it partially dissociates into phosphorus trichloride and chlorine

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

When, however, the pressure of either the phosphorus trichloride vapour or of the chlorine is increased, the dissociation of the gas is diminished and the vapour density is increased. The same is true for ammonium chloride, which does not dissociate to so large an extent when ammonia or hydrochloric acid is added to its vapour in the same way.

The effect of change of temperature and pressure on the condition of equilibrium has also been carefully studied for many partially dissociated gases. The particular state of equilibrium which is attained by any reacting system of substances, depends on the physical conditions to which the system is subjected, but the extent by which the state of equilibrium

is altered by change of temperature and pressure varies very largely according to the nature of the special reaction concerned. It may be taken as a general law that rise of temperature tends to produce such a change in the equilibrium of the system as is attended by an absorption of heat, whilst a lowering of the temperature has an effect in the opposite direction. Thus when a gas such as nitrogen peroxide, N_2O_4, is heated to a definite temperature it decomposes to a perfectly definite extent into molecules of the simpler gas, NO_2, a change which is accompanied by absorption of heat. If now the temperature be raised, the effect is to increase the dissociation of the gas, since thereby an absorption of heat and a consequent fall of temperature is produced. If a reaction proceeds without much evolution or absorption of heat, the effect of change of temperature on the condition of equilibrium is correspondingly small.

The effect of temperature on a chemical reaction is therefore of two kinds. In the first place it increases the velocity of the reaction, and in the second place it alters the final state of equilibrium which is attained. This is well illustrated in the case of hydrogen and iodine, which has been very thoroughly investigated by Lemoine[1] and Bodenstein.[2] When these two elements are heated together at 290°, several weeks are required for the establishment of equilibrium in which condition 16·37 per cent. of the total hydrogen is present in the free state; at 448°, on the other hand, the state of equilibrium is reached in a few hours, 23·63 per cent. of the total hydrogen being free.

In the same way increase of pressure produces such a change in the condition of equilibrium as is attended by a diminution of volume. Thus when the external pressure on such a gas as nitrogen peroxide is increased, whilst the temperature is maintained constant, the dissociation of the gas is diminished, this change being accompanied by a diminution of volume,

$$N_2O_4 = NO_2 + NO_2.$$

This is shown by the following numbers obtained by E. and L. Natanson[3] at a temperature of 49·7°.

[1] *Ann. Chim. Phys.* 1877, [5], **12**, 145.
[2] *Zeit. Phys. Chem.* 1896, **13**, 56.
[3] *Ann. Chim. Phys.* 1885, **24**, 454; 1886, **27**, 656.

Pressure.	Vapour density.
26·80 mm.	1·663
93·75	1·788
182·69	1·894
261·37	1·993
497·75	2·144

On the other hand increase of pressure produces no change in the equilibrium of a gas such as hydriodic acid at any particular temperature, the decomposition of this substance being unattended by any change of volume.

$$2HI = H_2 + I_2.$$

SPECTRUM ANALYSIS

61 THE following pages contain a short statement of the principles of spectrum analysis, and of the application of these principles to the detection of certain elementary and compound bodies. A complete treatise on spectrum analysis would here be out of place; for the subject has not only now outgrown the space which can be assigned to it in a work like the present, but much diversity of opinion is still expressed on various important points, and a discussion of these views cannot here be attempted.

The spectroscope, next to the balance, is the most useful and important instrument which the chemist possesses. Although it has only been employed for chemical investigations since the year 1860, it has been the means of effecting some of the most striking discoveries of modern times. By the help of the spectroscope the chemist is able to investigate the composition of terrestrial matter with a degree of exactitude previously undreamt of, and the discovery of the following new elementary bodies, as well as many members of the group of rare earths, may be considered as the first-fruits of the employment of this instrument in chemical analysis:

Cæsium and Rubidium, by Kirchhoff and Bunsen.
Thallium, by Crookes.
Indium, by Reich and Richter.
Gallium, by Lecoq de Boisbaudran.
Helium, by Ramsay.

In addition to this, the application of the methods of spectrum analysis to the investigation of the nature of the light emitted by the heavenly bodies has opened out a completely new field of research, and has laid the foundations of a new science, that of *Celestial Chemistry*. Such has been the progress

made in this direction that we are now not only assured of the existence of many of our well-known terrestrial metals in the atmospheres of the sun and the fixed stars, but we have gained a knowledge of the physical condition of our luminary such as we formerly could not have thought possible, and have even been able to form a definite opinion concerning the physical and chemical constitution of the nebulæ.

Moreover, it would appear that the time is not far distant when the results of spectrum observations may lead to most interesting and important conclusions respecting the molecular condition of matter, especially at temperatures far exceeding those to which our experiments have hitherto been confined, and to spectrum analysis we must also turn for assistance in our endeavours to answer the important question, Are the elements really undecomposable bodies? The subject is still under examination, but as yet the evidence adduced of the compound nature of the elements is not of a sufficiently conclusive character to warrant its introduction into these pages.[1]

62 The principles upon which spectrum analysis is founded are simple enough. When any solid or liquid bodies are gradually heated they will all be seen to become luminous at some temperature. If the light which these bodies emit, when they begin to glow or become luminous, be examined by means of a prism, and suitable optical arrangements, we observe that the rays of least refrangibility, viz. the red rays, are first seen and that, as the temperature rises, light of greater refrangibility is gradually emitted, until at last the body gives off blue or violet rays. When this point is reached the substance appears to the naked eye to be white-hot, as all the differently coloured rays, when brought together on to the retina produce the effect which we term white light. It is thus clear that the spectrum of every incandescent solid or liquid is the same, a bright continuous coloured band, whose rays extend without a break through all the colours of the rainbow from red to violet. The case is, however, quite different with gases glowing at a high temperature. The light which these bodies emit does not consist, within a certain limit, of light of all degrees of refrangibility. The spectrum of a glowing gas, instead of being continuous, is more or less broken up. Incandescent gases only emit rays of definite degrees of refrangibility, and their

[1] "Discussion of the Working Hypothesis that the so-called Elements are Compound Bodies," *Pro. Roy. Soc.* Dec. 12, 1878, **28**, 157.

spectra consist, therefore, of bright lines whose position undergoes no change when the temperature is increased. Thus the vapour of sodium emits a yellow light and its spectrum is characterised by a double yellow line having wave-lengths of 5895 and 5889 ten-millionths of a millimeter, and being coincident with the dark lines in the solar spectrum termed by Fraunhofer the D lines. These two bright sodium lines do not alter their position when the temperature of the vapour is raised; sodium vapour, as soon as it becomes luminous, glows with a yellow light, and by no increase of temperature can it be made white-hot. The peculiar colour of incandescent sodium

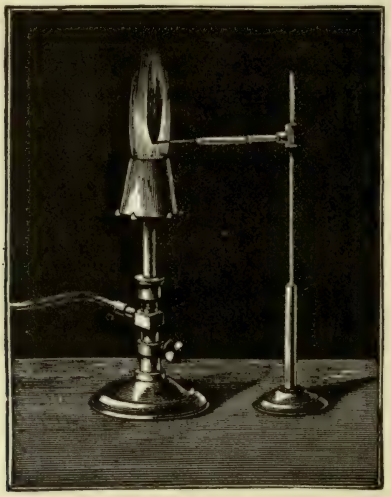


FIG. 4.

vapour is best seen by placing, in the non-luminous gas-flame, a small bead of chloride of sodium fused on to the end of a fine platinum wire. The salt volatilises, and the flame is coloured intensely yellow (Fig. 4).

63 Melville, in 1752, was the first to notice this yellow sodium flame, but he was unacquainted with its cause. In the year 1822, Sir David Brewster introduced his monochromatic lamp, the first idea being, however, due to Melville. In this same year Sir John Herschel investigated the spectra of many coloured flames, especially those obtained by means of the chlorides of copper and strontium, as well as by boracic acid, and in 1827 he writes concerning these observations—"the

colour thus contributed by different objects to flame affords in many cases a ready and neat way of detecting extremely minute quantities of them." Again, Fox Talbot writes as follows in 1826:—"The red fire of the theatres gave a most beautiful spectrum, with many lines or maxima of light. In the red these lines were more numerous, and crowded with dark spaces between them, besides an exterior ray greatly separated from the rest, and probably due to the nitre in the composition. In the orange was one bright line, one in the yellow, three in the green, and several that were fainter." The extreme delicacy of the sodium reaction and the universal distribution of this element were facts unknown to Talbot, and he consequently attributes the yellow line first to sulphur and afterwards to the presence of water. He adds, "if this opinion"—as to the cause of the production of the lines—"should prove correct and applicable to the other definite rays, a glance at the prismatic spectrum of a flame might show it to contain substances which it would otherwise require a laborious chemical analysis to detect." In 1834 Talbot again writes:—"Lithia and strontia are two bodies characterised by the fine red tint which they communicate to the flame. Now it is very difficult to distinguish the lithia-red from the strontia-red by the naked eye, but the prism betrays between them the most marked distinction which can be imagined. The strontia flame exhibits a great number of red rays well separated from each other by dark intervals, not to mention an orange and a very definite bright blue ray. The lithia exhibits one single red ray. Hence I hesitate not to say that optical analysis can distinguish the minutest portions of these two substances from each other with as much certainty as, if not more than, any known method."

In the year 1845 Dr. Wm. Allen Miller published the results of experiments on the spectra of coloured flames, together with drawings, but owing to the fact that in these researches a luminous flame was made use of, the representations of the several spectra are wanting in clearness and individuality. Swan was the first to point out that the bright yellow line coincident with Fraunhofer's D, which was seen in every flame, is caused by the presence of sodium salts, and it is to him that we are indebted for the discovery of the extreme delicacy of the sodium reaction, and for the proof of the universal distribution of this element.

The earliest observations of the spectra of metals which cannot be volatilised at the temperature of the non-luminous gas-flame were made in 1835 by Wheatstone. He allowed electric sparks to pass between poles of different metals, and found that the spectra of the sparks thus obtained were dissimilar. From this he concluded that the electric spark resulted from the volatilisation of the metal of the poles. "These differences," he says, "are so obvious, that one metal may easily be distinguished from another by the appearance of its spark; and we here have a mode of discriminating metallic bodies more ready than that of chemical examination, and which may hereafter be employed for useful purposes."

In 1855 Ångström thoroughly investigated the nature of the electric spark, proving the important fact that the spark yields two superimposed spectra; one derived from the metal of the pole, and the other from the gas or air through which the spark passes.

The results obtained by the above-mentioned observers were, however, but little known, and the method was never applied to the solution of problems in analytical chemistry, until the year 1860, when Bunsen and Kirchhoff began their classical researches. It is to these two philosophers that we must in truth ascribe the discovery of the spectrum analytical method, for they were the first to bring to bear upon this subject the sound principles of modern research, and to establish it upon the firm foundation of exact experiment.[1] Their labours soon met with their reward. A new alkali metal (cæsium) was almost immediately discovered,[2] and the presence of various well-known metals in the solar atmosphere was at the same time ascertained beyond doubt.[3]

[1] Kirchhoff and Bunsen, "Chemical Analysis by Spectrum Observations," Memoir I. *Phil. Mag.* 1860, [4], **20**, 89; ditto, Memoir II. *Phil. Mag.* 1861, [4], **22**, 329, 498.

[2] *Berlin Acad. Ber.* May 10, 1860; *Chem. News*, 1861, **3**, 132.

[3] *Berlin Acad. Ber.* Oct. 27, 1859; *Phil. Mag.* 1860, [4], **19**, 193.

CONSTRUCTION AND USE OF THE SPECTROSCOPE

64 The construction and arrangement of the spectroscope best suited to ordinary chemical purposes is shown in Fig. 5. This instrument consists of a prism (*a*) fixed upon a firm iron stand,

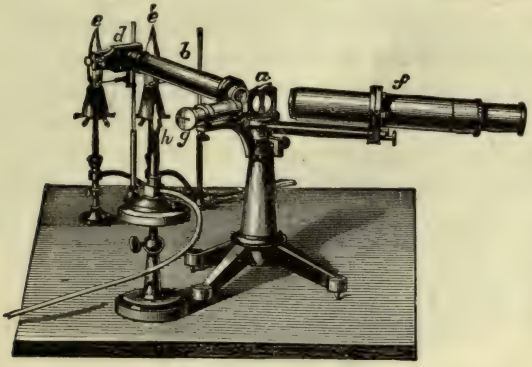


FIG. 5.

and a tube (*b*) called a collimator, carrying the slit (*d*), seen on an enlarged scale in Fig. 7, through which the rays from the coloured flames (*e* and *é*) fall upon the prism, being rendered parallel by passing through a lens placed at the other end of

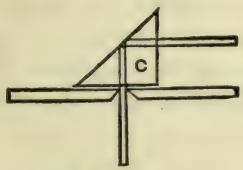


FIG. 6.

the tube. The light, having been refracted by the prism (*a*), is received by the telescope (*f*), and the image magnified before reaching the eye. The rays from each flame are made to pass into the telescope (*f*); one set (from *e*) through the upper uncovered half of the slit, the other (from *é*) by internal or total reflection from the sides of the small prism (*c*, Figs. 6

and 7), through the lower half; thus bringing the two spectra into the field of view at once, so that any wished-for comparison of the lines may be made. The small luminous gas-flame (*h*, Fig. 5) is placed so as to illuminate a fixed scale contained inside the tube (*g*); this is reflected from the surface of the prism (*a*) into the telescope, and serves as a means of measuring the position of the lines. The object of the superposition of the spectra is evident: it is to enable us to see whether the substance under examination really is the body which it is supposed to be. For instance, if we place a small quantity of a substance which we know to contain sodium in the one flame, and some of the substance to be tested in the other, and then send the spectra of these two flames into the telescope one above the other by means of the small reflecting prism placed on the end of the slit, we see at the same time the spectrum of the pure sodium compound and the spectrum supposed to be that of sodium; and we can

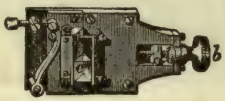


Fig. 7.

readily observe whether the lines coincide. If they coincide, and the two spectra have these lines exactly continuous one below the other, then we are quite certain that sodium is present.

65 Another and more complete form of spectroscope, used by Kirchhoff and especially adapted for physical research, is represented in Fig. 8. In this instrument the rays pass through four flint-glass prisms, and the dispersion is consequently much greater and the spectrum much longer than when only one prism is used. The intensity of the light is, however, much weakened by passing through these prisms, and hence this form of spectroscope, although the most accurate, can only be employed when the source of light is of considerable intensity.

An improvement has been made by the construction of spectroscopes provided with illumination-scales, which are divided and numbered so as to permit of the direct determination of the wave-length of any region of the visible spectrum.

The scale is similar to that shown in Fig. 9. It gives

wave-lengths in fractions of $\frac{1}{1000}$ of a millimeter, in accordance with the determinations of Ångström. The divisions of the scale enable the observer to read directly to the second place of decimals, and to estimate the third place.

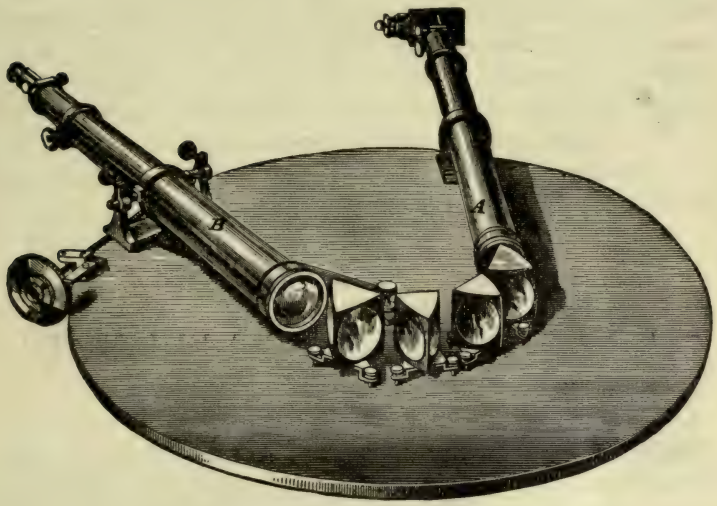


FIG. 8.

Thus the wave-length of Fraunhofer's line E is, according to Ångström, 0·0005273 mm. or μ0·5273. In an instrument made by Zeiss of Jena, the observer would at once see that the line was placed between divisions 52 and 53, and he would determine

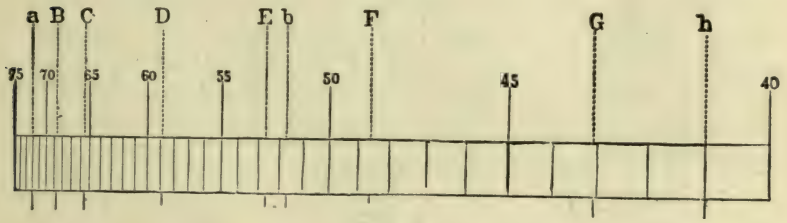


FIG. 9.

the fraction of the division to within one-tenth, but probably much nearer; the reading would probably be 52·7, which would give him the wave-length μ0·527. As a result of many observations it has been found that the mean error in the case of unexperienced observers is not greater than $\pm$ 0·000001 of a milli-

meter. In the regions of the spectrum with a lower wave-length than E the error is less.

Many other forms of spectroscope adapted for more accurate measurements are now in use, the illuminated scale being discarded and a divided circle and vernier provided for the exact determination of the angular dispersion and hence the wave-lengths of the various lines.

Greater accuracy in definition and wider dispersion are attained by the substitution of a diffraction grating for the prism, and such gratings, which contain from 200 to 4,000 lines per millimeter, are always employed for the most accurate work, when the source of light is of sufficient intensity

METHODS OF PRODUCING EMISSION SPECTRA

In order to obtain the peculiar spectrum of a chemical substance it is necessary that the light be examined which this substance emits in a state of glowing gas. The method which must be employed for this purpose differs according as the substance is solid, liquid, or gaseous.

Flame-Spectra

66 Slightly volatile substances, such as the salts of the metals of the alkalis and alkaline earths, may be placed upon a fine platinum wire, and this then brought into the non-luminous Bunsen flame. The salts there volatilise, the flame becomes tinged of a characteristic colour, and this coloured flame, when examined by the spectroscope, exhibits the peculiar spectrum of the given substance

Spark-Spectra

67 Again, when the substance is non-volatile at the temperature of the non-luminous flame, as is the case with most metals, and requires a much higher temperature to convert it into gas, either a powerful electric spark or the electric arc must be employed. The arrangement used for obtaining the spectra

of metals by means of the electric spark is seen in Fig. 10. It is only necessary to allow a powerful and bright spark to pass between poles made of the metal in question to obtain the characteristic bright-line spectrum of the metal, although it is to be remembered that the bright lines of the gases through which the spark passes (the air lines) will likewise be observed.

Another method of examining spark-spectra with especial regard to the easy chemical detection of the difficultly volatile metals has been proposed by Bunsen.[1]

The spark passes between two small cones of pure porous carbon, these having been impregnated with a solution of a

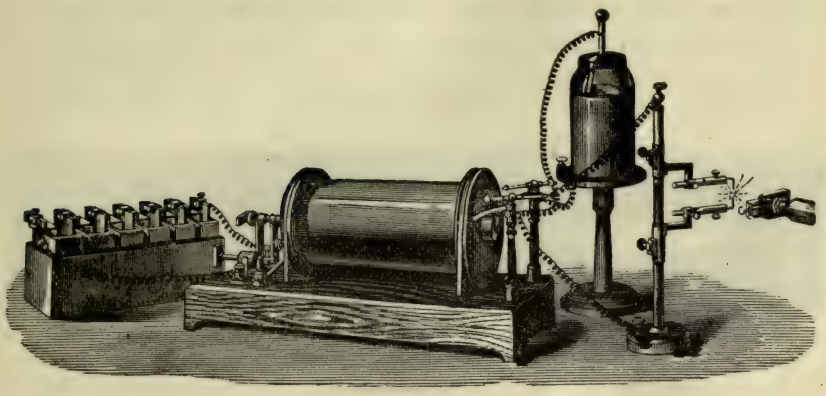


FIG. 10.

pure compound of the metal under examination. The advantages of this spark-spectrum method is well shown in the case of the detection of the rare allied metals cerium, lanthanum and didymium; yttrium and erbium. The chlorides of these metals do not volatilise at the temperature of the non-luminous flame, but yield well-defined and characteristic spark-spectra by which they can, without difficulty, be recognised.

Another method which is of special value for observing the spectra given by the soluble salts of the metals has been perfected by Lecoq de Boisbaudran. It consists in connecting the solution of the salt with the negative wire from the induction coil and then passing the spark from a positive pole of platinum placed just above the surface of the liquid. This

[1] *Phil. Mag.* 1875, [4], **50**, 418, 527.

method has proved of great value in the examination of the compounds of the rare earths.

If the body be a gas at the ordinary temperature the gaseous particles can be made to glow, and then to emit the rays which are peculiar to them, by passing an electric discharge through them. The colour of the electric spark or discharge will then be found to vary according to the nature of the gas, and an examination by means of a spectroscope of the light then emitted reveals the characteristic spectrum of the gas. The examination of the spectra of gases at low pressures is effected by means of *Geissler's Tubes* (Fig. 11). These contain the gases in a highly rarefied condition, and are furnished with platinum or aluminium wires melted through the glass, and as the rarefied gases offer little resistance to the passage of the electricity, the discharge passes readily through a long narrow tube, heating up in its passage the particles of gas, and thus producing a column of brightly luminous gas. The vapours of

FIG. 11.

liquids which are easily volatilised can also be examined in this way.

The spectra of gases at the ordinary pressure or under increased pressure can be observed by passing a spark as described above between metal poles in an atmosphere of the gas at the required pressure. It must be remembered that in such experiments the lines due to the metallic poles are also seen.

When the invisible portions of the spectrum are to be examined, it must be remembered that glass is much less transparent to the infra-red rays than to ordinary light and is almost opaque to ultra-violet. These last are, however, transmitted by quartz prisms and lenses, and then can be photographed or rendered visible by means of a screen coated with some phosphorescent substance such as platinocyanide of barium or potassium. The infra-red spectrum is best obtained by means of a metallic diffraction grating.

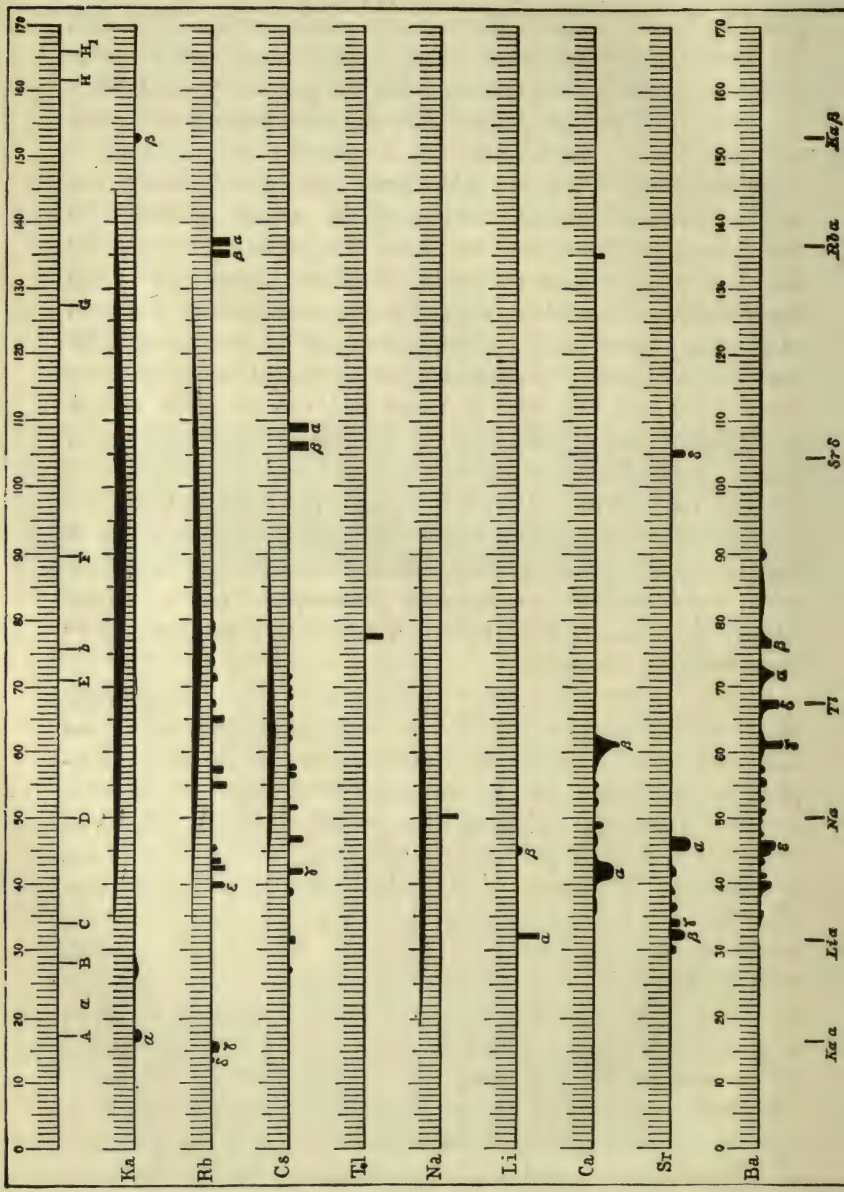
MAPPING SPECTRA.

68 The following method of mapping spectra has been proposed by Bunsen, and by this means persons unacquainted with the special appearances of individual spectra may soon learn to recognise the individual metals. "For the purpose of facilitating the numerical comparison of the data of various spectrum observations, we give in Fig. 12 graphical representations of the observations which are taken from the guiding lines given in the chromo-lithograph drawings of the spectra published in our former memoirs, and in which the prism was placed at the angle of minimum deviation. The ordinate edges of the small blackened surfaces, referred to the divisions of the scale as abscissæ, represent the intensity of the several lines, with their characteristic gradations of shade. These drawings were made when the slit was so broad and the flame of such a temperature that the fine bright line upon the broad Ca *α* band began to be distinctly visible.

"This breadth of the slit was equal to the fortieth part of the distance between the sodium line and the lithium line *α*. For the sake of perspicuity, the continuous spectra which some bodies exhibit are specially represented on the upper edge of the scale, to the divisions of which they are referred as abscissæ."

In order to ascertain the wave-lengths of the various lines observed it is necessary to draw a curve which represents the dispersion of the particular instrument which is being employed. This is done by selecting a number of lines as standard lines and plotting the wave-lengths of these as ordinates, and their positions on the scale of the instrument as abscissæ. The curve joining the points thus obtained can then be used for determining the wave-length of a line observed at any position on the scale. The most accurate method, however, of recording the spectrum given by any substance is to allow the image of the spectrum to fall upon a photographic plate, which is contained in a holder fitting into a camera which replaces the eye-piece of the telescope. The great advantage of the photographic method is that it is thus possible to determine with great accuracy the positions of a much larger number of lines than can be done by mere

observations with the eye, very faint lines being recorded when the time of exposure is increased. This is shown by the fact that in the portion of the spectrum from wave-lengths 3900 to 4100 (expressed in xth. meters, *i.e.*, 1×10^{-10}



meters) the number of lines of twelve metals noted by Lockyer is 416 as against 39 lines observed by Thalén. The photographic method can moreover be extended to those portions of the spectrum which are invisible to the eye. Photographs have thus been taken which extend to wave-length 12500 beyond the red and to 1852 beyond the violet.

VARIATION OBSERVED IN SPECTRA.

69 The nature of the spectrum emitted by a gas depends upon the temperature and pressure to which the gas is subjected. When an electric discharge of low intensity is passed through a highly rarefied gas, in a Geissler tube, the spectrum usually consists of a series of broad bright bands, which are made up of a great number of very fine lines crowded closely together, and are termed channelled-spectra (Plücker). The band spectrum of the discharge in the neighbourhood of the positive pole is moreover often different from that near the negative pole. At a higher temperature, produced by a discharge of greater intensity, the spectrum consists of bright lines. Finally when the pressure is increased, under certain conditions, many gases are found to give continuous spectra.

In like manner hydrogen, when examined by the ordinary electric spark, or in a Geissler's tube, yields a spectrum which consists of four lines, viz:

H α	coincident with Fraunhofer's line	C	in the red . . .	wave-length	6563
H β	,, ,,	F	,, bluish-green	,,	4861
H γ	,, ,,	G	,, indigo . .	,,	4341
H δ	,, ,,	h	,, violet . .	,,	4101

The lines H α, H β, and H γ are seen to be very bright when the gas is rarefied to a certain point; but if this rarefaction be carried on further the line H α gradually disappears, whilst H β, though fainter, remains well defined. If on the other hand, the intensity of the spark is increased, the lines H β and H γ begin to broaden, and when the tension of the gas is increased to 360 mm., and a Leyden jar is introduced into the circuit, the bright lines are found to give way to a continuous spectrum.

The relations with oxygen and nitrogen are still more complicated.

These variations in the spectra are probably due to some corresponding variation in the molecular constitution of the gas, and the further examination of the question is therefore of fundamental importance.

THE SPECTRA OF THE ELEMENTS.

70 If we compare the spectra of the various elements obtained according to one or other of the above methods, we find that each element, yields a characteristic spectrum, consisting of a larger or smaller number of bright lines, and that no two elements have even a single line in common.

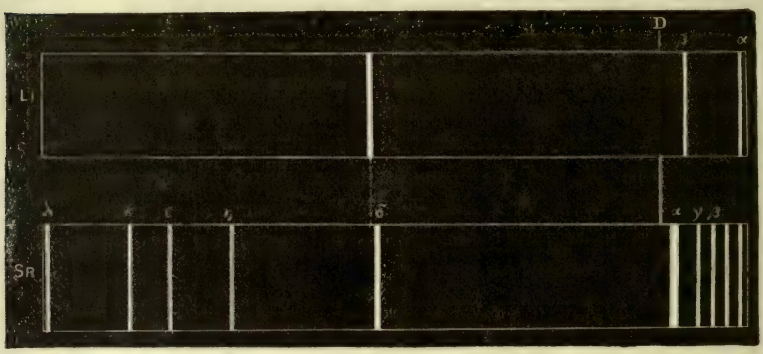


FIG. 13.

These lines do not undergo any alteration in relative position, or in degree of refrangibility, when the temperature is increased. The sodium double yellow line D is always seen at the same position of the spectrum, viz., wave-lengths 5896 and 5890, to whatever temperature the vapour may be raised. The *number* of lines visible in any given spectrum, as well as their relative intensities, may, on the contrary, undergo considerable changes dependent upon the temperature of the glowing gas, the pressure to which it is subjected, and the thickness of the incandescent layer. Thus, for example, the spectrum of lithium, as obtained by placing some salt of the metal in a non-luminous gas-flame, consists of one very bright red line, Li. α, w. l. 6708, and a very faint orange line, Li. β, w. l. 6104. Fig. 13. If, however, the spectrum of lithium, obtained

by placing some of its salts in the electric arc, or even in the oxyhydrogen flame, be examined, a new and splendid blue line (Li. γ), having a wave-length of 4602, makes it appearance, along with several others of less intensity, making in all twenty lines. The same phenomenon is observed in the case of the strontium spectrum (Fig. 13), where no less than four new lines (ϵ, χ, η, κ, and λ) make their appearance on increasing the temperature of the incandescent vapour of the metal.

A very important feature of the spark spectra of the metals was first observed by Lockyer, making use of a method in which the image of the electric arc formed by the incandescence of the metal was projected by a lens on the slit of the spectroscope. By this process he was enabled to examine the spectrum of various portions of the arc, and was thus led to the remarkable discovery that in each metallic spectrum certain lines are not only brighter and more intense than others, but are also *longer* than the rest. That is, that one line of a given metal is seen to stretch across from pole to pole, whilst another line only appears in the neighbourhood of the poles where the temperature is highest, and the density of the incandescent gas might be supposed to be greatest. These longest lines in the spectrum of a metal are the ones which exist in the spectrum produced at lower temperatures.

SPECTRA OF COMPOUNDS.

71 It appears probable that every individual compound possesses a characteristic spectrum. It is, however, impossible in many cases to observe this, because the compound is decomposed before it reaches a sufficiently high temperature to produce a spectrum. Thus when the compounds of one of the alkali metals are introduced into a Bunsen flame the spectrum produced is the same whatever the compound of the metal which is introduced, and consists of lines which are all found in the spark spectrum of the metal. On the other hand the different salts of barium, calcium, or strontium yield different spectra, and these moreover scarcely contain a single line which occurs in the actual spectrum of the metal. Thus if a bead of calcium chloride be brought into the flame a reddish tint is observed, caused by the volatilisation of the salt. The spectrum of this

coloured flame consists of a series of differently coloured broad bands, whose position is indicated by No. 1, Fig. 14, and which are mainly due to the unaltered chloride and the oxide formed from it by calcination. If, now, the same bead be placed between two metallic poles, and a bright electric spark be allowed to strike round the bead, the spark is seen to assume a bright-red tint, and when this coloured spark is observed by

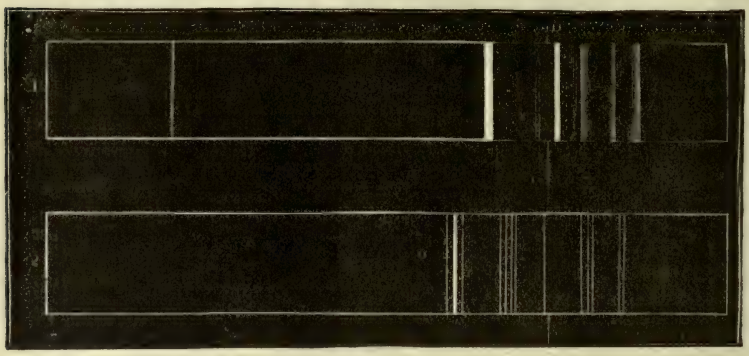


FIG. 14.

means of a spectroscope a spectrum of fine bright lines, shown in No. 2, Fig. 14, is seen. In the first instance the spectrum is that of incandescent calcium compounds; in the second it is that of the metal itself.

RELATIONS BETWEEN THE LINES OF A SPECTRUM.

72 Many attempts have been made to discover whether any relations exist between the wave-length of the lines in the spectrum of a given element, or between the spectra of allied elements. It appears from the work of Liveing and Dewar, Hartley, Lecoq de Boisbaudran, and especially of Kayser and Runge[1] that such relations do undoubtedly exist. The last named investigators have found that the spectra of the various elements can each be divided into two or three series of lines,

[1] *Nature*, 1895, **52**, 106; *British Ass.* 1888, 1895; *Wied. Annalen*, 1894, **52**, 114.

and that the individual lines of each of these series are connected by a definite numerical relation. This is expressed by the equation

$$\frac{1}{\lambda} = A - Bn^{-2} - Cn^{-4}$$

in which λ is the wave-length, A, B, and C are constants determined from the observations, and n takes the values of the successive whole numbers.

With some of the elements, such as lithium, the lines of each series are single, but in others such as sodium, potassium, rubidium, cæsium, copper, silver, aluminium, iridium, and thallium, the lines occur in groups of two; with others again, such as magnesium, calcium, strontium, zinc, cadmium, mercury, manganese, in triplets and sometimes in even more complicated groups. Thus in the spectrum of magnesium there is a characteristic group of three green lines, and this triplet is reproduced in the ultra-violet portion of the spectrum no less than ten times, the difference between the wave-lengths of the three members of the group being the same in every case. Not only do the lines belonging to the spectrum of a particular element appear to be connected in this way, but the spectra of allied elements also seem to show various analogies when examined in this manner.

This mode of examining the spectrum of an element has led to interesting results in the case of helium. The spectrum of the gas known by this name contains no less than six series of lines, those of each series being connected with each other by the equation given above. As this is twice as many series as are possessed by any other element, Runge and Paschen[1] concluded that the gas contains two distinct elements, three of the series belonging to the spectrum of each gas. Diffusion experiments were instituted to test this point, and the results so far obtained appear to show that two elements, one lighter than the other, are actually present. Our knowledge of the whole question of the relations between the separate lines of a spectrum and between the spectra of different elements is still in a very rudimentary state, although the question is one of the most interesting in the whole field of chemical and physical inquiry.

[1] *Nature*, 1895, **52**, 520.

APPLICATION OF THE SPECTROSCOPE TO CHEMICAL ANALYSIS.

73 This instrument is especially valuable in the ordinary qualitative analysis for the detection of the metals of the alkalis and alkaline earths, and of the more recently discovered metals thallium, indium, and gallium, inasmuch as the salts of the above metals can be volatilised in the non-luminous gas-flame. The following extract from Bunsen and Kirchhoff's memoir on this subject gives some idea of the ease and accuracy with which the presence of certain of these metals can be detected, and leads to the conclusion that the sodium salts are universally distributed:

"The following experiment shows that the chemist possesses no reaction which in the slightest degree will bear comparison as regards delicacy with this spectrum analytical determination of sodium. In a far corner of our experiment room, the capacity of which was about sixty cubic meters, we burnt a mixture of three milligrams of chlorate of sodium with milk sugar, whilst the non-luminous colourless flame of the lamp was observed through the slit of the telescope. Within a few minutes the flame, which gradually became pale yellow, gave a distinct sodium line, which, after lasting for ten minutes, entirely disappeared. From the weight of sodium salt burned and the capacity of the room, it is easy to calculate that in one part by weight of air there is suspended less than $\frac{1}{20,000,000,000}$ of a part of soda smoke. As the reaction can be observed with all possible comfort in one second, and as in this time the quantity of air, which is heated to ignition by the flame, is found to be only about 50 cub. cent. or 0·0647 grm. of air, containing less than $\frac{1}{20,000,000,000}$ of sodium salt, it follows that the eye is able to detect with the greatest ease quantities of sodium salt less than $\frac{1}{3,000,000}$ of a milligram in weight. With a reaction so delicate, it is easy to understand why a sodium reaction is almost always noticed in ignited atmospheric air. More than two-thirds of the earth's surface is covered with a solution of chloride of sodium, fine particles of which are continually being carried into the air by the action of the waves. These particles of sea-water cast thus into the atmosphere evaporate, leaving almost inconceivably small residues

which floating about, are almost always present in the air, and are rendered evident to our eyes in the sunbeams. These minute particles perhaps serve to supply the smaller organised bodies with the salt which larger animals and plants obtain from the ground. In another point of view, however, the presence of this chloride of sodium is of interest. If, as is scarcely doubtful at the present time, the explanation of the spread of contagious disease is to be sought for in some peculiar contact action, it is possible that the presence of so antiseptic a substance as chloride of sodium, even in almost infinitely small quantities, may not be without influence upon such occurrences in the atmosphere.

"By means of daily and long-continued spectrum observations it would be easy to discover whether the alterations of intensity in the line Naα produced by the sodium in the air have any connection with the appearance and the direction of march of an epidemic disease.

"The unexampled delicacy of the sodium reaction explains also the well-observed fact, that all bodies after a lengthened exposure to the air show the sodium line when brought into a flame, and that it is only possible in a few salts to get rid of the line even after repeated crystallisation from water which has only been in contact with platinum. A thin platinum wire freed from every trace of sodium salt by ignition, shows the reaction most visibly on allowing it to stand for a few hours in the air; in the same way the dust which settles from the air in a room shows the bright line Naα. To render this evident it is only necessary to knock a dusty book, for instance, at a distance some feet from the flame, when a wonderfully bright flash of the yellow band is seen."

In like manner the metal lithium before the year 1860 was known only to exist in a few rare minerals. It is now ascertained that lithium compounds are most widely distributed, occurring not only in every mineral spring, but in river- and sea-water, in the juices of almost every plant, and even in human blood and muscular tissue.

74 Again, to quote from Bunsen's Memoir: "Minerals containing lithium, such as triphylline, triphane, petalite, and lepidolite require only to be held in the flame in order to obtain the bright line in the most satisfactory manner. In this way the presence of lithium in many felspars can be directly detected; as, for instance, in the orthoclase from Baveno. The line is

only seen for a few moments, directly after the mineral is brought into the flame. In the same way the mica from Altenburg and Penig was found to contain lithium, whereas micas from Miask, Aschaffenburg, Modum, Bengal, Pennsylvania, &c., were found to be free from this metal. In natural silicates which contain only small traces of lithium this metal is not observed so readily. The examination is best conducted as follows: A small portion of the substance is digested and evaporated with hydrofluoric acid or fluoride of ammonium, the residue moistened with sulphuric acid and heated, the dry mass being dissolved in absolute alcohol. The alcoholic extract is then evaporated, the dried mass again dissolved in alcohol, and the extract allowed to evaporate on a shallow glass dish. The solid pellicle which remains is scraped off with a fine knife, and brought into the flame by the thin platinum wire. For one experiment $\frac{1}{10}$th of a milligram is in general quite a sufficient quantity. Other compounds besides the silicates, in which small traces of lithium require to be detected, are transformed into sulphates by evaporation with sulphuric acid or otherwise, and then treated in the manner described.

"In this way we arrive at the unexpected conclusion that lithium is most widely distributed throughout nature, occurring in almost all bodies. Lithium was easily detected in forty cubic centimeters of water of the Atlantic Ocean, collected in 41° 41′ N. latitude and 39° 14′ W. longitude.

"Ashes of marine plants (kelp) driven by the Gulf Stream on to the Scotch coasts contain evident traces of this metal. All the orthoclase and quartz from the granite of the Odenwald which we have examined contains lithium. A very pure spring water from the granite in Schleierbach, on the west side of the valley of the Neckar, was found to contain lithium, whereas the water from the red sandstone which supplies the Heidelberg laboratory was shown to contain none of this metal. Mineral waters, in a liter of which lithium could hardly be detected according to the ordinary methods of analysis, gave the line Liα even if only a drop of the water on a platinum wire were brought into the flame. All the ashes of plants growing in the Odenwald on a granite soil as well as Russian and other potashes contain lithium.

"Even in the ashes of tobacco, in vine-leaves, in the wood of the vine and in the grapes, as well as in the ashes of the

crops grown on the Rhine plains near Wäghausel, Deidesheim, and Heidelberg, on a non-granite soil, was lithium found. The milk of the animals fed on these crops also contains this widely diffused metal."

The special details of the spectra of the metals of the alkalis and alkaline earths will be found under the description of each metal.

75 *Discovery of New Elements.* The discovery by Bunsen of two new alkali metals found in the mineral water of Dürkheim,[1] was one of the first results of the application of the spectroscope to chemical analysis. Both of these new elements are contained in the mineral water in extremely small quantities, so that 44,000 kilos. of the water had to be evaporated in order to obtain 16·5 grams of the mixed chlorides. The first of these new metals yields a spectrum distinguished by two splendid bright blue lines, and hence the name *Cæsium* (*cæsius*, the blue colour of the sky) was given to it. The second new metal is characterised by a spectrum which contains a bright red line less refrangible than the potassium line Kα, and also a line in the violet. As the red line is the one by which the presence of this metal can be most readily and certainly detected, Bunsen give to it the name of *Rubidium* (*rubidus*, dark-red).

Since the discovery of these two bodies by Bunsen in 1860, chemists have recognised the presence of both these metals in very varied situations; one of them, rubidium, being comparatively widely distributed, and found in very many mineral waters. Thus, for example, the celebrated water[1] of Bourbonne-les-Bains contains 0·032 grm. of chloride of cæsium, and 0·010 grm. of chloride of rubidium in one liter of water; whilst in the well-known springs of Vichy, Gastein, Nauheim Karlsbrunn, and many more, either one or both of these new metals have been discovered. Rubidium has been found to be more widely diffused than cæsium, occurring in animate as well as in inanimate nature. It has been found in beetroot, in tobacco, in the ash of the oak (*Quercus pubescens*), in coffee, in tea, and in cocoa. In their general chemical characters, as in their spectroscopic relations, these two new metals exhibit the closest analogy with potassium. So much so is this the case, that without the aid of the spectroscope and the differences which the spectra of these three metals present, it was absolutely impossible to distinguish between them. Chemists had, in

[1] An analysis of this water is found at p. 298 of vol. i.

fact, experimented upon cæsium but had mistaken it for potassium.

A rare mineral called *Pollux* occurs in the island of Elba. This mineral was analysed in the year 1846 by the well-known chemist Plattner, and by him it was supposed to contain potassium. In calculating out the results of his analysis, Plattner invariably found a considerable loss, the cause of which he was unable to ascertain. Spectrum analysis has now explained this anomaly, for since the discovery of the two new metals it has been found that it was not potassium, but the new metal cæsium, which was present, of the oxide of which no less than 34 per cent. is contained in this mineral. The want of agreement of the former analysis is wholly attributable to the difference between the combining weights of these two bodies, that of potassium being only 38·85, whilst that of cæsium is 131·9 : and if this last number be used the analyses calculate, as they ought to do, to 100 parts.

Soon after the discovery of the new alkali metals by Bunsen, Crookes, in 1861, proved the presence of a third new metal in a seleniferous deposit from a sulphuric acid chamber at Tilkerode in the Harz. To this new element he gave the name of *Thallium*, from *thallus*, a young twig, owing to the bright green colour which this substance and its compounds impart to the non-luminous flame. The spectrum of thallium is a simple one, consisting of one bright green line (Tl *a*), having a wave-length of 5,349 ten-millionths of a millimeter. Thallium has since been shown to be frequently contained in iron-pyrites and several other minerals. so that it is a somewhat widely distributed element. It exhibits very remarkable and interesting chemical properties. In certain respects it closely resembles the metals of the alkalis. In others in more nearly approaches the heavy metal lead. Hence thallium has very appropriately been termed by Dumas the ornithorhynchus amongst the metals.

A fourth new metal was discovered in the year 1864, by Reich and Richter, in Freiberg. They gave to this substance the name of *Indium*, owing to the fact that it imparts a dark-blue or indigo tint to the flame, and its spectrum consists of two indigo-coloured lines. It has been found, although in small quantities only, in the zinc-blendes from Freiberg, Goslar, and a few other places.

In 1875, Lecoq de Boisbaudran, found a fifth new metal in zinc-blendes from the Pyrenees. To this substance he gave the

name of *Gallium*. Its spectrum consists of two violet lines, which are best seen in the electric spectrum. The brightest of these lines has a wave-length of 4170; the second line, which is fainter, having a wave-length of 4040.

The application of spectrum analysis to the study of the rare earths has made us acquainted with a very large number of new substances, among which may be mentioned scandium, ytterbium, and samarium, although it is not yet certain that all of these are individual substances. Of surpassing interest is the discovery by Ramsay of helium in the gas evolved by the action of sulphuric acid on clèveite, a rare uranate of uranyl, lead, and the rare earths. The gas evolved in this reaction was supposed by certain observers to be nitrogen, but an examination of its emission-spectrum showed that this differs entirely from that of nitrogen, and is characterised by a double yellow line of wave-length 5875 which occupies the same place in the spectrum as a double dark line in the solar spectrum. This solar line had been previously observed, and since it did not coincide with a bright line of any known element had been ascribed by Lockyer to an element which he named helium, since it occurred in the sun but not in the earth. Further investigations have shown that the gas in question contains this solar element, probably mixed with some other substance (p. 137).

ABSORPTION-SPECTRA.

76 In accordance with the important optical law known as the law of exchanges, every incandescent body is capable of absorbing, at the same temperature, exactly those kinds of rays which it emits. Hence a glowing body which yields a continuous spectrum exhibits, at the same temperature, a continuous absorption, whilst those bodies whose emission-spectra are broken or discontinuous yield, under similar conditions of temperature, absorption-spectra which are in like manner broken or discontinuous. This selective absorptive action of glowing gases is strikingly shown in the case of sodium vapour. If a small piece of this metal be burnt in an iron cup in front of the slit of the spectroscope the bright yellow sodium lines will at first be seen, but they will soon be replaced by two dark lines which are exactly coincident with the bright

yellow lines, and are seen upon a background of a bright continuous spectrum (Fig. 15). The sodium spectrum has thus been *reversed*, inasmuch as the yellow rays in passing through the sodium vapour have been absorbed, whilst the particles of glowing oxide of the metal yield a continuous spectrum. Sodium vapour

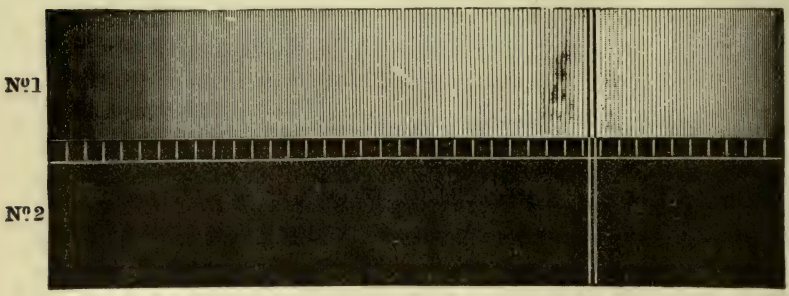


FIG. 15.

is opaque to the yellow D rays. In a similar way the bright lines of the emission-spectra of lithium, calcium, strontium, barium, as well as of magnesium, copper, and several other heavy metals, have been reversed, or the absorption-spectra of these metals have been obtained. The numerous fine black

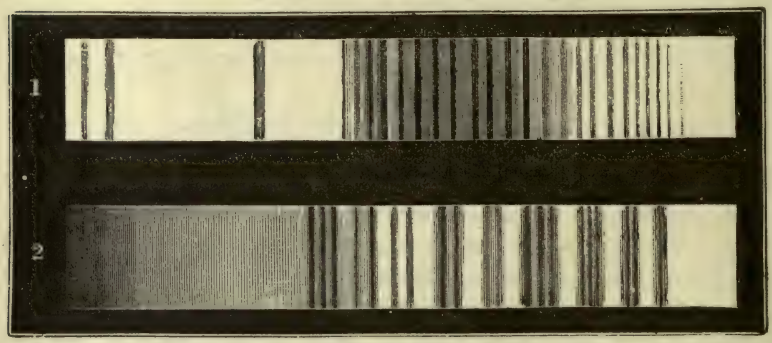


FIG. 16.

lines seen in the solar spectrum and known as *Fraunhofer's lines*, are produced by the reversal of the spectra of hydrogen, sodium, calcium, iron, magnesium, and other metals which are present in the state of luminous gas in the solar atmosphere.

This selective absorption is exhibited by certain liquid and solid bodies, as well as by gases, at the ordinary temperature of

the air, and this property serves as a means of detecting the presence of the substances in question. The dark absorption bands seen when white light passes through the vapour of iodine (No. 1, Fig. 16) and those first observed by Brewster in the red fumes of nitrogen peroxide (No. 2, Fig. 16) are good examples of this selective absorptive power of gases.

The arrangement shown in Fig. 17 is one which may be used for examining the absorption-spectra of gases by means of a direct-vision spectroscope. Even some colourless gases, such as aqueous vapour, possess a strong power of selective absorption when a column of sufficient depth is examined (Rain-band).

It has been shown that when we examine the absorption-spectra of two gases having the same density and colour,

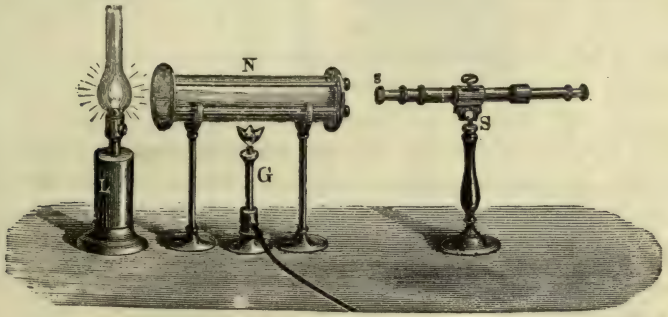


Fig. 17.

such as bromine and iodine monochloride, we find that although their spectra present a general analogy, they are not identical. The absorption-spectra of the vapours of potassium and sodium have also been mapped. The absorption-spectrum of a substance is not, as a rule, identical with the emission-spectrum of the same body when examined at a lower temperature than that at which the bright line spectrum is obtained. Thus the dark absorption bands seen in iodine vapour are not identical with, or even analogous to, the bright lines of the emission-spectrum of iodine. This indicates that in the one case we have to do with a molecular condition different from that existing in the other case.

One of the most striking cases of absorption in the case of liquids is seen in solutions of salts of the metal didymium. All these nearly colourless salts possess the power of absorbing

certain rays, so that if a small glass trough filled with a very dilute solution of a didymium salt be placed in front of the slit of the spectroscope and diffuse day-light or the light from a luminous gas-flame be allowed to pass through the solution into the spectroscope, two dark bands are seen in the luminous continuous spectrum. These lines are so characteristic and are produced by so small a quantity of didymium salt that this reaction serves as the most delicate as well as the most easy test for the presence of this metal.

Many coloured metallic solutions, such as chromium salts, permanganates, and uranium compounds, exhibit similar powers of selective absorption, and the bands thus produced may serve as a means of detection of the substances in question. Nevertheless the chemist is bound to use circumspection in arguing from the mere inspection of absorption-spectra, for these are by no means so certain or unfailing in their indications as the unaltering bright lines of the emission-spectra. This conclusion is borne out by the experiments of Bunsen on the didymium spectra. He has shown that the various compounds of this metal do not exhibit exactly the same absorption bands, and that the crystallographic direction in which the ray of light passes through a crystal of a didymium salt exerts a marked influence on the arrangement of the dark bands. Even a variation in the amount of free acid present in the solution of a salt also gives rise to marked differences.

Metallic solutions are not the only liquids which exhibit this power of selective absorption. Many organic liquids possess this power in a high degree, and by this means complicated liquids of animal and vegetable origin can be easily distinguished when no other method can be employed. As an example of selective absorption in organic liquids, the spectrum reaction of the blood may be cited. No. 1, Fig. 18, exhibits the two dark bands, situated between Fraunhofer's D and E, seen in oxidised blood and due to oxyhæmoglobin. No. 2 on the same figure shows the absorption-spectrum of deoxidised or venous blood, consisting of one dark band. By the action of an acid on blood the oxyhæmoglobin is converted into hæmatin yielding a different absorption-spectrum. The hæmatin, like the oxyhæmoglobin, is capable of undergoing oxidation and reduction. The absorption bands of hæmatin are shown in Nos. 3 and 4, Fig. 18. Another interesting fact with regard to blood-spectra is that the blood when it contains very small

quantities of carbon monoxide in solution exhibits a very peculiar set of absorption bands. Carbon monoxide acts, how-

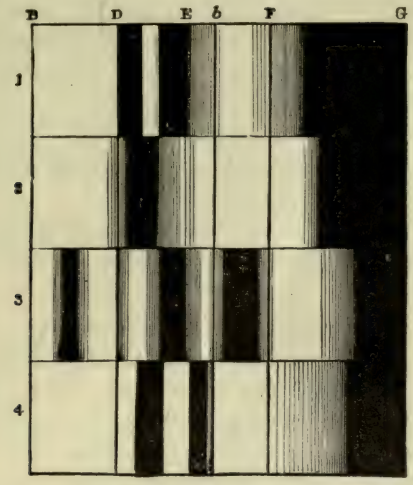


FIG. 18.

ever, as a very violent poison, and these peculiar bands are seen in the blood of animals which have been suffocated in the

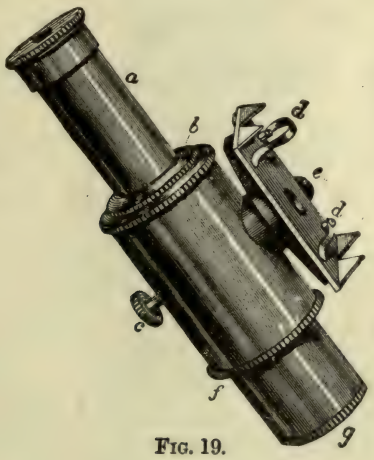


FIG. 19.

fumes of burning charcoal. In the same way the peculiar compound which hæmoglobin forms with hydrocyanic acid yields a characteristic absorption-spectrum. The instrument

with which these absorption-spectra can be observed with extremely small quantities of the liquids is a spectroscope placed in connection with a microscope. Fig. 19 shows the construction of such an instrument. The eyepiece contains prisms so arranged that the refracted rays pass in a straight line from the object into the eye. Such spectroscopes are termed direct-vision instruments, and are very portable and useful forms of the apparatus. This instrument, in the hands of Sorby, has proved capable of detecting $\frac{1}{1000}$ part of a grain of blood in a blood-stain.

The same observer states that wines of different vintages may be distinguished by a variation in their respective absorption-spectra.[1]

Many substances which are transparent to ordinary light show very characteristic absorption bands in the ultra-violet or infra-red portions of the spectrum. Thus Hartley[2] has shown that the aromatic compounds are characterised by well-marked absorption bands in the ultra-violet, the position of the bands being different for different compounds, whilst Abney and Festing[3] have ascertained the position of the bands and lines produced in the infra-red spectrum by many elements and groups of elements or radicals.

COMPOSITION OF THE SOLAR ATMOSPHERE.

77 When sunlight is allowed to fall upon the slit of a spectroscope, the solar spectrum thus obtained is observed to differ essentially from the spectra which we have hitherto considered. A bright band is seen stretching from red to violet, but this band is cut up by a very large number of fine black lines. These lines are always present, and always occupy the same relative position in the solar spectrum—they are, in fact, shadows in the sunlight. They were first noticed by Wollaston, but first carefully mapped by Fraunhofer, the principal lines being designated by him with the letters of the alphabet. Fig. 20 is a reduced facsimile of Fraunhofer's original map.

The cause of these dark solar lines was long a mystery.

[1] *Chem. News*, 1869, p. 295.
[2] *Journ. Chem. Soc.* 1885, i. 685; 1888, i. 641.
[3] *Proc. Roy. Soc.* 1881, **31**, 416; 1881, **32**, 258.

Fraunhofer finding that sunlight, both direct and reflected as moonlight always gave the same lines, whereas the light of the

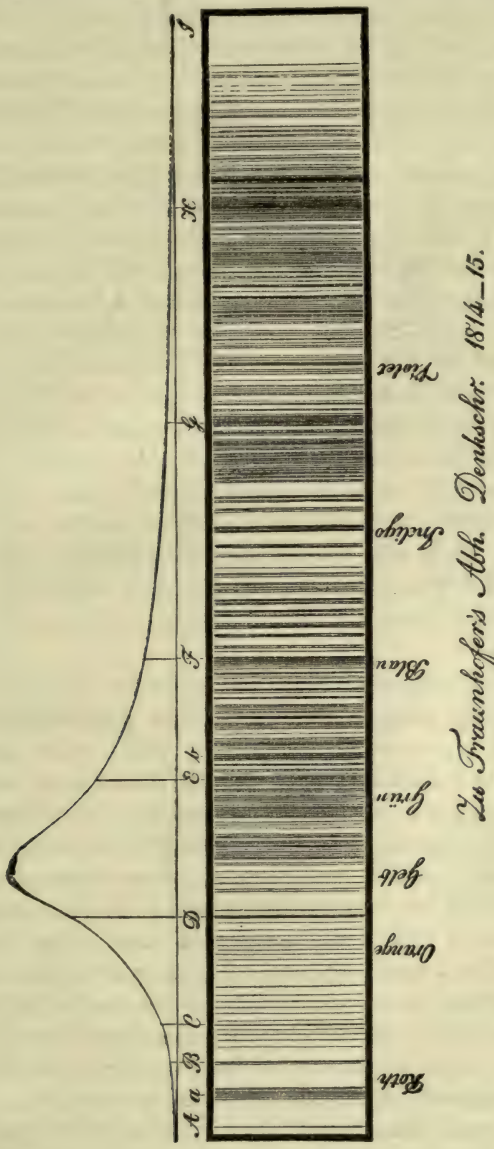


Fig. 20.

Fraunhofer's Abh. Denkschr. 1814–15.

fixed stars contained different dark lines, came to the conclusion in 1814 that these dark lines were produced in the solar

atmosphere, and not by the light passing through the intervening space, or through our own atmosphere.

It was not until the year 1860 that the true cause of the production of these lines was first clearly proved by Kirchhoff, not, however, before the same cause had been suggested as a possibility by Stokes. Kirchhoff was engaged in the comparison of the bright lines of certain metallic spectra with the dark lines in the sun. To his astonishment he found that *all* the bright lines of such metals as iron, calcium, and magnesium have dark representatives in the solar spectrum. Not only has each bright metal line a dark one coincident with it, but the breadth and intensity of the bright metal line is as a rule reproduced in the dark line in the solar spectrum, so that if a solar and a metal spectrum be allowed to fall one below the other in the field of the telescope, *all* the bright lines of the metal are seen to be coincident with dark lines. Other metals, such for instance as gold and antimony, exhibit no such coincidences. Not one single bright line of these is found coincident with a dark solar line. Hence it is clear that there must be some kind of connection between the bright lines of these metals and the dark solar lines. Such coincidences cannot possibly be the result of mere chance. The coincidence of the *dark* solar lines with the *bright* iron lines is caused by the presence of iron in the sun's atmosphere.

We have already seen that the spectrum of sodium can be reversed. By passing the light from incandescent sodium through the vapour of the metal the bright yellow double line is changed to a dark one. If the solar atmosphere contain the vapours of sodium, of iron, of magnesium, of calcium, &c., in the state of glowing gas, and if white light from the incandescent mass beneath pass through these vapours, the effect produced would be exactly that which is in fact observed.

"As this is the only assignable cause, the supposition appears to be a necessary one. These iron vapours might be contained either in the atmosphere of the sun or in that of the earth. But it is not easy to understand how our atmosphere can contain such a quantity of iron vapour as would produce the very distinct absorption-lines which we see in the solar spectrum; and this supposition is rendered still less probable by the fact that these lines do not appreciably alter when the sun approaches the horizon. It does not, on the other hand, seem at all unlikely, owing to the high temperature which we

must suppose the sun's atmosphere to possess, that such vapours should be present in it. Hence the observations of the solar spectrum appear to me to prove the presence of iron vapour in the solar atmosphere with as great a degree of certainty as we can attain in any question of physical science" (Kirchhoff).

By observing the coincidences of these dark lines with the bright lines of terrestrial metals, we arrive at a knowledge of the occurrence of such metals in the solar atmosphere. The metals whose existence in the sun has now been ascertained, thanks to the labours of Kirchhoff, Ångström, Thalén, Lockyer, Kayser, Runge, and Rowland, are the following:

Elements contained in the Sun's Atmosphere.

Aluminium.	Helium.	Rhodium.
Barium.	Hydrogen.	Scandium.
Beryllium.	Iron.	Silicon.
Cadmium.	Lanthanum.	Silver.
Calcium.	Lead.	Sodium.
Carbon.	Magnesium.	Strontium.
Cerium.	Manganese.	Tin.
Chromium.	Molybdenum.	Titanium.
Cobalt.	Neodym.	Vanadium.
Copper.	Nickel.	Yttrium.
Erbium.	Niobium.	Zinc.
Germanium.	Palladium.	Zirconium.

Presence Doubtful.

Iridium.	Platinum.	Thorium.
Lithium.	Potassium.	Tungsten.
Nitrogen.	Ruthenium.	Uranium.
Osmium.	Tantalum.	

STELLAR SPECTRA.

78 In a similar way Drs. W. Allen Miller and Huggins have succeeded in proving that the elements hydrogen, sodium, calcium, magnesium, iron, bismuth, tellurium, antimony, and mercury occur in the atmosphere of the star Aldebaran, whilst others stars have been shown to contain other elements.

More recently Dr. Huggins has applied the photographic mode of record to the spectra of stars, and has obtained permanent pictures of the dark lines in the stellar spectra drawn by nature herself.

From the observations of Secchi and Vogel, it appears that the stars may be divided into three main classes according to the general nature of the spectra which they present. In those of the first class metallic vapours are absent from the atmosphere of the star, or if present have only a very slight absorptive power. The spectra of such stars are characterised by four dark lines corresponding in position to the bright lines of hydrogen, as is the case in Sirius, Vega and most white stars, or by faint dark metallic lines unaccompanied by strong hydrogen lines, or again by bright hydrogen lines as well as the bright helium line (α Lyra, γ Cassiopeia). The second group contains the yellow stars such as Pollux, Capella, Aldebaran, &c., the spectra of which resemble that of the sun, containing numerous dark lines due not only to hydrogen but also to metals. The members of the third group, which comprises the red and blue stars such as Betelgeux and α Hercules, in addition to some dark lines show channelled-space spectra, which are probably due to the presence of chemical compounds in their atmospheres. Some of the stars of this group appear to contain some compound of carbon in the incandescent state.

The simpler a spectrum is, the simpler must be the composition of the body which yields that spectrum. Arguing upon these premisses, Lockyer concludes that the atmospheres of the whiter stars contain the fewer elements and those of smaller atomic weight, and that as the peculiar colour of the star becomes more distinct its atmosphere becomes more complicated. These results, coupled with the well-known fact that dissociation of chemical compounds uniformly takes place if the temperature be only sufficiently high, has led Lockyer to suggest that the heat being greatest in the whitish stars, their simple spectra can be best explained by the existence of a temperature sufficient to dissociate the substances to which on this earth we give the name of elementary bodies.[1]

[1] For further information see Roscoe's *Lectures on Spectrum Analysis*, fourth edition, Macmillan and Co., 1885; Lockyer's *Chemistry of the Sun*, Macmillan and Co.; and also *Proc. Roy. Soc.* 1887, p. 37; 1888, p. 117.

SYSTEMATIC DESCRIPTION OF THE METALS AND THEIR DERIVATIVES.

79 In the following systematic description of the metals, the latter are classified in groups according to the periodic system, each of these groups being further divided into two or more sub-groups. In general the members of each sub-group are described in order of their atomic weight, but in certain cases, where the elements of higher atomic weight are of greater importance, these are described first; thus, for example, the description of sodium and potassium precedes that of lithium.

GROUP I.

Sub-group (*a*).—The Alkali-Metals.

Lithium
Sodium
Potassium
Rubidium
Cæsium

Sub-group (*b*).—The Copper Group.

Copper
Silver
Gold

The metals of this group all form characteristic series of salts in which the metal is monovalent, and except in the case of copper and gold this series of salts is by far the most important. The division into sub-groups is more sharply defined than is usually the case, the metals copper, silver and gold, which as already pointed out fall in the centre of the 'double periods' (p. 47), only showing a limited resemblance to the alkali metals. The resemblance is most prominent in the case of the two typical elements, sodium and lithium, the salts of which are frequently isomorphous with the corresponding silver salts. In the exact

classification according to the periodic classification, sodium belongs to the sub-group (*b*), as like copper, silver and gold it is a member of one of the "odd" periods; in its properties, however, it so closely resembles the metals of the sub-group (*a*) that it is always described together with these.

THE ALKALI-METALS.

80 The above name is given to this group because the two most important members, sodium and potassium, are constituents of the substances which have been long known by the name of *alkalis*. The name alkali is first found in the works of the Latin Geber, and is the name there given to the soluble salt obtained by the lixiviation of the ashes of sea-plants. We also find the same word employed to designate the carbonate of potash obtained by a similar treatment of the ashes of land-plants. The difference between the alkalis potash and soda was at that time not understood, and in order to distinguish them from the carbonate of ammonia, the volatile alkali, they were both termed the fixed alkali. The distinction between the mild and caustic alkalis had long been known, and the mode of converting the former into the latter by boiling their solutions with lime was a well-recognised process. In the Historical Introduction (see vol. i. p. 15) we have seen that Black, in the year 1755, was the first to explain this change, as he proved that the mild alkalis contain fixed air or carbon dioxide.

The first clear distinction between the two alkalis, potash and soda, appears to have been made by Duhamel in the year 1736, although Stahl pointed out that the alkali contained in common salt is different from that contained in wood-ashes, and this difference was indicated by the first being termed the mineral and the second the vegetable alkali. Marggraf showed in 1759 that the salts of the two alkalis possess totally distinct properties, and that whilst those of the common alkali tinge the flame of a spirit-lamp violet, those containing the base of common salt impart to the flame a yellow colour. It was, however, soon afterwards pointed out by Klaproth that the vegetable alkali potash was contained in several minerals, such as leucite, and then the special name *potash* in English, *potasse* in French, and *kali* in German was given to this particular alkali. Klaproth suggested for the mineral-alkali the name *natron*, the

English equivalent for which is *soda*, and the French *soude*. All these names had formerly been used indiscriminately for any alkali.

Up to the year 1807 the alkalis were considered to be simple substances. Lavoisier had indeed expressed a view that these bodies probably contained oxygen, owing to their analogy with other well-known metallic oxides, but Davy was the first to isolate the metals.

A few years later (1817), the lithium compounds were discovered by Arfvedson, and in 1860 the two remaining metals, rubidium and cæsium, were isolated by Bunsen and Kirchhoff.

The alkali metals are all soft silvery metals, which may be readily fused and volatilised, the melting and boiling points becoming lower with increasing atomic weight. The specific gravity increases with the atomic weight but less rapidly than the latter, the atomic volume therefore becoming greater as we ascend the series. They are the most strongly electro-positive of the metals, their hydroxides being the most powerful bases known, and within the group itself the basicity increases with the atomic weight, that of cæsium hydroxide being the greatest.

The alkali metals form only one series of stable salts, and in these they are monovalent; a few halogen derivatives are known in which they are tri- or pentavalent, but these readily decompose into the free halogens and the monovalent haloid compound of the metal. With very few exceptions the whole of the salts are soluble in water, those of lithium being the least soluble.

They combine with oxygen to form oxides of the general formula M_2O, which correspond to the monovalent salts; these are however scarcely known in the free state, as they combine very readily with water forming the characteristic hydroxides MOH, which are also produced by the direct action of the metals on water. Sodium and potassium also form well-defined peroxides having the formulæ Na_2O_2 and K_2O_4 respectively.

SODIUM. Na = 22·87.

81 In the writings of the Old Testament (Jeremiah ii. 22) we find a substance used for washing purposes mentioned as *nether*. This same substance is mentioned in Proverbs as being one which effervesces when vinegar is poured over it, and in our version this substance is called nitre. In Luther's translation

the name chalk is given to this body, but there can be little doubt that by the word *nether* was meant trona, or the native carbonate of soda, to which the names *νίτρον* in Greek and *nitrum* in Latin were applied.

At a later date the name *nitrum* was given to saltpetre; but up to the fourth century there is no doubt that nitrum signified the carbonate of soda originally obtained from the salt lakes in Egypt, to which the names *flos salis* and *spuma nitri* were given. Reasons for believing this are, amongst others, the facts stated by Pliny, that in the first place this nitrum does not decrepitate when thrown on the fire ("igni non exsilit nitrum") as saltpetre does; that, secondly, it possesses a fatty touch, this property being heightened by boiling it with lime; thirdly, that the nitrum is used both with and without oil in the baths (in balneis utuntur (nitro) sine oleo); and fourthly, that it is largely used in the manufacture of glass.

The word nitrum was, as we have already remarked, long indiscriminately applied to both soda and potash. The history of the distinction between these two bodies has also been dwelt upon. The terms soda and natron came into general use in the fifteenth century to distinguish fixed alkali from nitre.

82 The sodium compounds occur very abundantly and are universally diffused. Vast quantities of sodium chloride, NaCl, are found in extended deposits as rocksalt in different parts of the world and in various geological formations, whilst the same compound occurs in solution in sea-water, salt lakes, salt springs, and many mineral waters. The double fluoride of sodium and aluminium, cryolite $3NaF, AlF_3$, is found in large quantity in Greenland, and sodium nitrate, or Chili saltpetre, $NaNO_3$, is deposited in beds several feet thick in the rainless districts of Southern Peru and Bolivia; the carbonate, Na_2CO_3, and the sulphate, Na_2SO_4, are found either in springs or as deposits in the beds of dried-up lakes. Many minerals, especially nepheline, sodalite, albite, labradorite, contain sodium silicate in considerable quantity, whilst traces of sodium compounds occur in all silicates. Indeed it is difficult to find any substance which does not contain traces of sodium, as evidenced by the very delicate spectroscopic reaction.

Sodium compounds are also found in living organisms of all kinds. Plants growing in or near the sea contain sulphate, iodide, and chloride of sodium. The whole of the animal body, especially the juices, is rich in sodium compounds, the carbonate,

chloride, and phosphate chiefly occurring, together with sodium salts of organic acids.

Sodium salts are, however, not characteristic of vegetable life in the same sense that potassium salts are. Thus, whilst the latter alkali is always present in larger quantities in certain organs of the plant than in others, sodium appears in general to be equally diffused throughout the whole organism. It is also a remarkable fact that the sodium salts contained in the ashes of plants are insoluble in water, as they combine with the phosphates of the alkaline earths to form insoluble compounds. For this reason the presence of sodium compounds in the ashes of plants has often been overlooked.

Duhamel and Cadet showed that if the plant *Salsola Soda*, which grows near the sea, and which yields an ash rich in soda salts, be transplanted to an inland situation, the ash gradually loses soda and gains in potash, until at last the whole of the former disappears. On the other hand, if inland plants are grown near the sea the reverse change takes place (Correnwinder).

83 *Preparation of Metallic Sodium.* Sodium, like potassium, was first obtained in 1807 by Davy [1] by electrolysis of caustic soda, though according to him it is less easily prepared in this way than potassium. Up to recent years sodium was manufactured by a process proposed by Brunner of igniting a mixture of carbonate of soda and charcoal, and this method was improved by Deville,[2] who showed that the manufacture of sodium is simpler and easier than that of potassium as there is no liability to explosions. This process, which is in principle the same as that described for the manufacture of potassium, is, however, a costly and an uneconomic one, inasmuch as a considerable quantity of the sodium is volatilised and burns; some adheres to the receiver, and the reduction does not occur completely, so that in a well-conducted operation the sodium obtained is only about one-third of the theoretical yield, and, moreover, as it is necessary to expose the retorts to a white heat, they are rapidly burnt through and rendered useless. An improvement in this method of manufacture was introduced by Castner [3] in 1886 by replacing the sodium carbonate by caustic soda. The reaction is expressed as follows:

$$6NaOH + 2C = 2Na_2CO_3 + 3H_2 + 2Na.$$

[1] *Phil. Trans.* 1808, pp. 5, 21. [2] *Ann. Chim. Phys.* 1855 [3], **43**, 5.
[3] See Roscoe, *Proc. Roy. Inst.* London, 1889.

By this process, which was successfully worked for some time, the price of sodium was materially reduced, but more recently Castner[1] has introduced another method of manufacture, viz., the electrolysis of caustic soda, which has placed the sodium industry on an entirely new basis, and obviated the great difficulties which necessarily beset all the older plans. The temperature of decomposition rises only a few degrees above 300°C.. and thus the wear and tear of the apparatus is reduced to a minimum, whilst at the same time the whole of the sodium is obtained as metal. In the year 1807 Davy, with his battery of 100 cells, found it "impossible to produce the effects of decomposition on pieces of soda of more than fifteen or twenty grains in weight"; the process has now been so amended that the plant at the works of the Aluminium Company, Limited, at Oldbury, manufactures about five tons of sodium per week.

The apparatus consists of an iron vessel *a* (Fig. 21) suitably

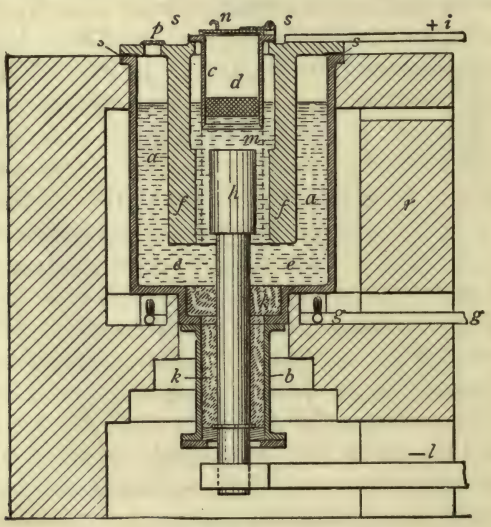


FIG. 21.

mounted in brickwork *r* so that the heat applied by the gas burners *g* may be well distributed. The vessel *a* is provided with one or more base pipes *b* adapted to receive the negative electrodes *h*, which are preferably of metal and pass up into the vessel. Suspended directly above the cathode is a tubular iron receptacle

[1] *Journ. Soc. Chem. Ind.* 1891, 777, Pat. No. 13,356 (1890).

c which is provided on its upper end with a lid *n*, whilst to its lower edges is secured an iron wire gauze *m*, which, when the receptacle *c* is placed in position, completely surrounds the cathode. The positive electrodes *f* are made of such metal as will withstand the oxidising action of the evolved gases, as, for instance, nickel, and either form part of the cover of the vessel *a* or are bolted to it, being so placed that when the cover is adjusted the electrodes are a suitable distance from and directly surround the gauze *m*. Electrical connection is made between the cover by the connection *i* with the positive pole of the dynamo, and by the connection *l* with the negative. The cover is provided with an opening *p* for the escape of gases resulting from the electrical action, this opening also serving for the introduction of a thermometer. Insulation is made at the points *ss*, by means of asbestos. The size and distance apart of the electrodes are both proportioned to the quantity of current to be supplied, the effective action of the apparatus being largely dependent on the accuracy with which this is carried out.

The sodium being much lighter than the hydroxide, rises together with the hydrogen from the negative electrode and passes into the receiver *c*, the hydrogen escaping around the edges of the cover *n*, while the molten metal continues to collect in quantity. From time to time this collected metal *d* is removed by means of a large finely-perforated spoon, the perforations enabling the molten caustic to flow out whilst the metal remains in the spoon. Caustic is added to the bath from time to time to replace the metal removed, and in this manner a continuous process may be carried on in an economical manner.

Any increase of temperature is followed by a proportionate loss of product and waste of electrical energy, but it is possible to so adjust the electrical current and the quantity of caustic alkali forming the electrolyte, that the proper temperature will be maintained in a previously melted bath without external heat, or even by an increase of current to melt the bath, subsequently reducing the quantity of current, until the working temperature is attained; if large currents are used the bath and the electrodes may be artificially cooled by air or water circulation. The cathode may be conveniently sealed in the extension *b* by means of molten caustic *k* which is allowed to harden before beginning the process.

In order to secure a fair yield of metal for the current applied

it is necessary that the temperature of the electrolyte should not be allowed to rise above 330°, or 20° above the melting point of caustic soda.

The sodium thus obtained is sufficiently pure for ordinary purposes, and only requires to be remelted and then cast into sticks about one inch thick and a foot long. These may be preserved in closed vessels in dry air for a long time without undergoing any considerable oxidation, but it is usual to first moisten the sticks with petroleum. When in smaller masses it is advisable to keep the sodium under petroleum.

84 *Properties.* Sodium is a white metal possessing a high silver-white lustre. It may be obtained in the crystalline condition by sealing up 100 grams of metal in a glass tube filled with hydrogen. The sodium is melted at one end of the glass tube and then allowed to filter through some wire gauze placed in a narrowed portion of the tube. The melted metal is thus rendered perfectly free from oxide, and must be fused in the clean part of the tube, allowed to cool partially, and then the central liquid portion suddenly poured off from the solidified crust. According to Long [1] sodium crystallises in the quadratic system, forming acute octohedra. The specific gravity of sodium at 0° was found by Davy to be 0·9348; later and more accurate determinations of Baumhauer give 0·9735 as its specific gravity at 13°·5. At −20° sodium is rather hard, at 0° it is very ductile, at the ordinary temperature it has the consistency of wax, at 50° it is semi-fluid, and it melts at 95°·6 (Bunsen), forming a liquid resembling mercury in its appearance. Sodium boils at 742°, [2] emitting a vapour which is colourless when seen in thin layers, but of a peculiar purple colour by transmitted light when seen in quantity (Roscoe and Schuster). With the exception of silver, copper, and gold, it conducts heat and electricity better than any of the metals (Matthiessen), and next to cæsium, rubidium, and potassium, it is the most electro-positive metal (Bunsen).

When freely exposed to moist air sodium oxidises like potassium, although not quite so rapidly. It burns with a bright yellow flame when heated in the air, forming the monoxide and the dioxide. Thrown on to cold water it swims on the surface, disengaging hydrogen and dissolving, but not evolving heat enough to ignite the hydrogen. Brought into contact

[1] *Journ. Chem. Soc.* 1861, 123.

[2] Perman, *Journ. Chem. Soc.* 1889, i. 328.

with hot water, or thrown on to a thick paste of starch, or wet filter paper, the evolved hydrogen ignites and burns with a yellow sodium-tinted flame.

Sodium is largely used for the manufacture of cyanides and sodium peroxide and for the preparation of silicon, boron, and magnesium, and of certain organic substances such as antipyrin. Sodium-amalgam has also been employed in the process of extracting gold from the quartzose rock in which it occurs, and this amalgam, like sodium itself, is of great service as a reducing agent in the laboratory.

Sodium forms with potassium an alloy which is liquid at the ordinary temperature, and looks like mercury. When it contains 16 parts of potassium to 10 parts of sodium this alloy becomes pasty at 8°, and solidifies at lower temperatures. If more potassium is contained in it the alloy remains liquid below 0°. The alloy is not only obtained by melting the two metals together under rock oil, but also by adding sodium to fused acetate of potassium when gases are rapidly evolved and the alloy formed (Wanklyn).

SODIUM COMPOUNDS.

Sodium and Oxygen.

85 Sodium forms two well defined oxides, a strong basic monoxide Na_2O, and a peroxide Na_2O_2. In addition to these a grey suboxide possibly exists, formed when a clear surface of the metal is first exposed to air, and also a sesquioxide Na_2O_3.

Sodium Monoxide, Na_2O. Sodium does not oxidise in perfectly dry air, but when heated in slightly moist oxygen it takes fire and burns with formation of a mixture of the monoxide and peroxide. If the amount of oxygen is limited and the sodium is heated above 180°, only the former oxide is obtained.[1]

It is a grey mass having a conchoidal fracture and has a sp. gr. of 2·805; it melts at a dull red heat and undergoes volatilisation at a still higher temperature (Davy). When brought in contact with water violent action occurs, sodium hydroxide being formed.

[1] Holt and Sims, *Journ. Chem. Soc.* 1894, i. 442.

Sodium monoxide is the oxide corresponding to the monovalent sodium salts, to which class as already stated, all the stable ones belong. They are characterised by the fact that almost all are readily soluble in water, even when the corresponding salts of the remaining alkali metals are sparingly soluble. The least soluble salt is sodium metantimonate.

Sodium Hydroxide, *Sodium Hydrate*, or *Caustic Soda*, NaOH. When water is added to sodium monoxide great heat is evolved, and the hydroxide is formed; it is also obtained when sodium is thrown on to water. In order to prepare it in this way a piece of clean sodium of the size of a small nut is thrown into a silver basin containing a few drops of water, and kept cool in cold water. A second piece of metal is then added, and a little more water, and so on, until about a pound of metal has been used. Great care is needed in this operation, as the fused soda is apt to be thrown about. The solution is evaporated and the soda obtained in a fused state and cast into sticks. The hydroxide thus obtained is free from chloride and sulphate of sodium, and from alumina, silica, and oxide of iron. It is however, an expensive material used only for special purposes in the laboratory.

In order to obtain it more cheaply it is prepared by boiling a solution of sodium carbonate with milk of lime:

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

and it is now also obtained by the electrolysis of a solution of sodium chloride, the sodium first liberated reacting with the water to form caustic soda with evolution of hydrogen. The manufacture by both of these methods will be described later, together with that of sodium carbonate (p. 214).

Commercial caustic soda prepared by the first method always contains sodium chloride and sulphate, and alumina, and frequently silica, and ferric oxide. It may be purified by dissolving in pure alcohol, and evaporating the clear solution to dryness in a silver basin (*Soude a l'alcool*, Berthollet). The product still contains traces of sodium chloride, carbonate and acetate, the latter being formed by the action of caustic soda on the alcohol.

Caustic soda is a white opaque solid, with a fibrous texture; it has a specific gravity of 2·13 (Filhol), melts at 310°, is

rather less volatile than caustic potash, and decomposes into its elements at the melting-point of cast iron.[1] It deliquesces in the air and when moist absorbs carbon dioxide, and acts as a powerful cautery. It is very soluble in water and in alcohol, one part dissolving in 0·47 parts of the former, yielding a strongly alkaline solution. The fused substance rapidly corrodes most metals, cast iron and silver being least affected.

Hydrated Caustic Soda, $2NaOH + 7H_2O$. This hydrate is deposited in large transparent tabular monosymmetric crystals when a solution of soda-ley of specific gravity 1·365 is exposed to a temperature of —8°. These crystals melt at 6°, yielding a liquid having a specific gravity of 1·405 (Hermes).[2] Hydrates of the formulæ $NaOH+2H_2O$, and $2NaOH+3H_2O$ are also known.

Soda-ley. The following table gives the specific gravity of soda-ley at 15°, according to the experiments of Schiff:[3]

Percentage of NaOH.	Specific Gravity.	Percentage of NaOH.	Specific Gravity.
1	1·012	30	1·332
5	1·059	35	1·384
10	1·115	40	1·437
15	1·170	45	1·488
20	1·225	50	1·540
25	1·279	55	1·591
		60	1·643

Caustic soda is a most useful substance, and is largely used for many industrial processes, its chief employment being in the manufacture of soap. A description of the methods used for its preparation on the large scale will be found in the sequel.

Sodium Dioxide, Na_2O_2 is formed when the metal is heated in an excess of air or oxygen, and is prepared on the large scale by placing sodium on aluminium trays, which are in turn placed on tram carriages passing through an iron tube heated to about 300°. The air is freed from moisture and carbonic acid before passing through the tube, and as the fully oxidised product is taken from the finishing end of the tube a fresh charge of sodium is placed at the other end, the tram carriages being

[1] Deville, *Compt. Rend.* 1857, **45**, 857.
[2] G. Rose, *Pogg. Ann.* 1863, **119**, 170.
[3] *Annalen*, 1858, **107**, 300.

pushed forward to admit the fresh trays. The finished product contains about 93 per cent. Na_2O_2. About 3·5 tons are manufactured per week by this process by the Aluminium Company, Oldbury, 2 tons of sodium being required for its production.

Pure sodium dioxide has a white colour, but the commercial product has usually a slight yellow tinge. It dissolves in water with partial formation of caustic soda and hydrogen dioxide, the latter decomposing on heating into water and oxygen, and an analogous decomposition takes place on addition of mineral acids, the corresponding sodium salt being formed. It does not give off oxygen, unless heated to very high temperatures, but acts as a very strong oxidising agent on any substance mixed with it, and is therefore used in the analysis of many minerals, such as iron pyrites, chrome ironstone, &c. It has a very violent action on glacial acetic acid, the whole mass becoming ignited, and in presence of moisture oxidises any readily combustible substances such as wood, paper, &c., and great care must therefore be exercised in dealing with large quantities of the dioxide.

It absorbs carbonic anhydride with formation of sodium carbonate and liberation of oxygen, and also absorbs carbonic oxide with formation of sodium carbonate, and nitrous and nitric oxides with formation of sodium nitrate.[1] When the solution in cold water is allowed to evaporate, large tabular hexagonal crystals of the hydrate $Na_2O_2+8H_2O$ separate out, which on standing over sulphuric acid lose water forming the hydrate $Na_2O_2+2H_2O$. The first hydrate is also formed when alcohol is added to a mixed solution of caustic soda and hydrogen peroxide.[2]

A solution of the dioxide in hydrochloric acid, consisting of sodium chloride and hydrogen dioxide, is now manufactured on the large scale and is much used for bleaching straw under the name of *soda bleach*. It is also sold in the solid form mixed with calcium or magnesium chlorides, which on addition of water yields a solution of hydrogen dioxide and the hydrated oxide of calcium and magnesium.[3]

Sodyl Hydroxide, NaO.OH. When sodium peroxide is treated with alcoholic hydrochloric acid or with absolute alcohol at 0° the dioxide partially dissolves and a white powder remains

[1] Harcourt, *Journ. Chem. Soc.* 1862, 276.
[2] Fairley, *Journ. Chem. Soc.* 1877, i. 125.
[3] Castner, *Journ. Soc. Chem. Ind.* 1893, 603.

which has the composition NaO_2H. It dissolves in water at 0°, forming a strongly alkaline solution, which on warming decomposes into caustic soda and oxygen, the same decomposition taking place with explosion when the dry substance is heated. It does not yield salts with mineral acids but yields with acetic acid an *acetate* $NaO.OC_2H_3O$ and must therefore contain the hydroxyl group. Its formation from the dioxide is represented by the equation :

$$Na_2O_2 + C_2H_5OH = NaOC_2H_5 + NaO.OH.$$

Sodyl hydroxide gives off oxygen on addition of potassium permanganate, evolves chlorine with hydrochloric acid, and liberates iodine from potassium iodide at the ordinary temperature.

Two constitutional formulæ are possible for this substance namely : Na.O.OH and O:Na.OH. It is not converted by hydrochloric acid into sodium hypochlorite, according to the equation

$$Na.O.OC_2H_3O + HCl = Na.O.Cl + C_2H_4O_2$$

but yields hydrogen dioxide, and therefore the second of these formulæ, according to which sodium is here present as a triad, is the more probable. In this case it appears not improbable that sodium dioxide itself contains both monad and triad sodium, as represented by the formula O:Na.O.Na.[1]

Sodium Trioxide, Na_2O_3 is formed according to Johannis,[2] by the action of an excess of oxygen on a solution of sodammonium in liquid ammonia. It is decomposed by water with evolution of oxygen and formation of the hydrated dioxide.

Sodium and Hydrogen.

86 *Sodium Hydride*, $(Na_2H)_n$. When dry hydrogen gas is passed over fused sodium at a temperature between 300° and 400° and under a pressure of 760^{mm}, the metal gradually absorbs 237 times its volume of hydrogen. The compound obtained possesses a metallic lustre and a silver-white colour; its specific gravity is 0·959; it is soft at the ordinary temperature

[1] Tafel, *Ber.* 1894, **27**, 816, 2297.
[2] *Compt. Rend.* 1893, **116**, 1370.

and fuses at a somewhat lower temperature than sodium. It may be fused in hydrogen without undergoing any decomposition, but when heated to 330° it begins to evolve hydrogen gas, and if heated in a Sprengel's vacuum pump, the whole of the hydrogen is given off. In this way Troost and Hautefeuille[1] were able to determine the composition of the compound. One volume of sodium disengaged 237 volumes of hydrogen; the volume required by the formula Na_2H being 238.

Sodium and the Halogens.

87 *Sodium Fluoride*, NaF, is prepared by neutralising aqueous hydrofluoric acid with caustic soda or sodium carbonate. It crystallises in cubes and sometimes in octohedra, has a specific gravity of 2·766, and melts at 902° (Carnelley). It is sparingly soluble in water, 100 parts of water dissolving 4 parts of the salt (Frémy).

Sodium Chloride, or Common Salt, NaCl. Davy states that sodium takes fire when brought into chlorine gas. Wanklyn[2] has, however, shown that dry chlorine does not attack sodium even in the melted state. Probably Davy's chlorine was moist. Metallic sodium also retains its brightness in liquid chlorine at −80°.

Chloride of sodium occurs as rock-salt in large deposits in various geological strata, in solution in sea-water and brine springs, and in small quantities in all running water. The chief European deposits of salt occur in the trias formation. The most important are those at Northwich and Winsford in Cheshire, at Weilizca in Galicia, at Reichenhall, Hallein, Berchtesgaden, and other localities in the Tyrol, and at Stassfurt in the north of Germany. Rock-salt also occurs in France, Spain, and Switzerland, and in Asia, Africa and America, in various localities.

The Cheshire salt-beds occur in the keuper (triassic) beds. They are two in number, separated by about thirty feet of clay; they are together about sixty yards thick, and extend over an area of sixteen miles by ten.

The methods adopted for raising and working the salt differ widely, according to the nature of the deposit and its situation.

[1] *Ann. Chim. Phys.* 1874 [5], **2**, 273.
[2] *Chem. News*, 1869, **20**, 271.

Sometimes the rock-salt is mined and brought up to the surface; generally, however, salt-springs or brine-wells are artificially constructed by sinking a bore-hole through the overlying strata to the salt-bed, and allowing water to pass down this boring. The water soon becomes saturated with salt, and it is then pumped up and the salt obtained by evaporation, either by means of fuel or by exposure to air.

Owing to the presence of cheap fuel and water carriage the quantity of salt raised in England is much larger than that obtained in any other country. No less than 1,821,978 tons of salt were obtained from English brine in the year 1891, and in addition 184,284 tons were raised as rock-salt.

The process of evaporating the brine, 100 parts by weight of which in Cheshire usually contain 23·3 parts of salt, is of the simplest kind. Indeed it has not been improved since the time of the Romans, and although very numerous patents for the purpose have been taken out, no economy in fuel has been effected. The brine is evaporated in large shallow iron pans heated by means of fires placed beneath. The appearance and quality of the salt which deposits depends upon the temperature at which the brine is kept and the rapidity with which the process of evaporation is conducted. The Cheshire brine contains about 1·65 per cent. of calcium sulphate, $CaSO_4$, and about 0·05 per cent. of magnesium chloride, $MgCl_2$. The first of these salts is deposited as pan-scale when the brine is boiled down.

In Germany, where fuel is dear, the brine is evaporated by exposing it to the action of the air by a process termed "graduation." After having been allowed to trickle several times over high walls of fagots and thus become more concentrated, it is boiled down in pans. The arrangement used for this purpose is shown in Fig. 22.

Preparation of Salt from Sea-water. The evaporation of sea-water in salterns, or brine-pans, by the aid of air and the sun's heat has been carried out from very early times. In England, at Hayling Island near Portsmouth, and at Lymington, and in Scotland at Saltcoats on the Ayrshire coast, such salterns have been in use quite recently.

In countries more favoured by sunshine, such as the coast of France, Portugal and Spain, these salterns are more numerous than with us. When this salt, termed Bay-salt, is deposited, a mother-liquor called Bittern is left. This consists of the

chlorides, sulphates, and bromides of magnesium and potassium, and from this bromine is obtained.

All common salt contains a small quantity of sodium sulphate, calcium sulphate, and magnesium chloride. The presence of the last compound renders the salt liable to become damp in the air. This same substance likewise not unfrequently

FIG. 22.

attacks the iron pans, causing the presence of traces of ferric chloride in the salt.

In order to prepare chemically pure sodium chloride from common salt, hydrochloric acid gas is passed into a saturated solution of salt. A precipitate of the pure chloride is thrown down, the alkali sulphates and magnesium chloride remaining

in solution. The precipitate is thrown on a filter, washed with concentrated hydrochloric acid, and then dried and fused in a platinum basin.

Properties.—Sodium chloride crystallises in cubes. Rock-salt is usually found in cubical crystals, sometimes, however, in octohedra and intermediate forms. It possesses an agreeable saline taste and a specific gravity at 0° of 2·16. Rock-salt is highly diathermanous, or it permits the heat-rays, dark as well as visible, to pass through it; hence it is a valuable substance in thermal researches. Sodium chloride melts at 815·4° (Meyer, Riddle, and Lamb), and begins to volatilise at temperatures not far removed from its melting point; hence it cannot be fused without loss (Stas).

When heated with silicic or boric acid, sodium chloride is decomposed, with liberation of hydrochloric acid and formation of a silicate or borate. It has been proposed to utilise the former of these reactions for the manufacture of carbonate of soda, but without practical success. Sulphuric acid decomposes it, hydrochloric acid, and hydrogen sodium sulphate or the normal sulphate being formed.

According to the experiments of Poggiale,[1] one hundred parts of water dissolve the following quantities of sodium chloride at the corresponding temperatures:

Temp.	0°	5°	14°	25°	40°	60°	80°	100°	109·7°
NaCl.	35·52	35·63	35·87	36·13	36·64	37·25	38·22	39·16	40·35

Hence sodium chloride is not, as was formerly supposed to be the case, equally soluble in cold and in hot water. The specific gravity of salt solutions of different strengths is, according to Gerlach,[2] as follows:

Percentage of NaCl.	5	10	15	20	25
Specific Gravity at 15°.	1·03624	1·07335	1·11146	1·15107	1·19228

Brine containing 26·27 parts of salt in 100 boils at 108·8° when the thermometer is placed in the liquid (Guthrie). Chloride of sodium is nearly insoluble in absolute alcohol.

When the temperature of a saturated solution of sodium chloride is lowered to − 10° a crystalline hydrate separates out[3]

[1] *Ann. Chim. Phys.* 1843, [3], **8**, 469.
[2] Gerlach, *Zeit. Analyt. Chem.* 1869, **8**, 279.
[3] Lowitz, *Crell. Ann.* 1793, i. 314.

having the composition $NaCl + 2H_2O$; this is also obtained by cooling a solution of sodium chloride in hot hydrochloric acid, in which it is sparingly soluble.[1] When brine is further cooled to − 22° acicular bundles of crystals separate out. These consist of the cryohydrate, which contains 23·7 per cent. of sodium chloride (Guthrie).[2]

Sodium Bromide, NaBr, and *Sodium Iodide*, NaI, are prepared by processes similar to those employed in the case of the corresponding potassium salts the latter being more largely used. Both crystallise from hot concentrated solution in anhydrous cubes, whilst if the solutions be allowed to evaporate at the ordinary temperature, monosymmetric prisms are deposited. These contain two molecules of water of crystallisation, and are isomorphous with the corresponding hydrate of sodium chloride.

Sodium Hypochlorite, NaOCl, is prepared by passing chlorine over powdered sodium carbonate, slightly moistened with water; it is however usually obtained in solution by passing chlorine into a solution of caustic soda, which yields a mixture of the chloride and hypochlorite

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O.$$

This was formerly known as chloride of soda or *Labarraque's liquor*.

Sodium Chlorate, $NaClO_3$. This salt is obtained, according to Muspratt and Eschelmann's process, by saturating milk of magnesia with chlorine and adding sodium carbonate to the resulting solution of magnesium chloride and chlorate. The liquor, after filtering from precipitated carbonate is boiled down, the sodium chloride fished out as it separates, and the sodium chlorate purified by recrystallisation. In Pechiney's process the solution of calcium chlorate and chloride obtained by passing chlorine into hot milk of lime is evaporated down and as much as possible of the calcium chloride removed by crystallisation, the liquid being then decomposed with salt-cake:—

$$CaCl_2 + Ca(ClO_3)_2 + 2Na_2SO_4 = 2CaSO_4 + 2NaCl + 2NaClO_3.$$

The solution is then evaporated and treated as in Muspratt and Eschelmann's process. According to the recent process of

[1] Bevan, *Chem. News*, 1877, **35**, 17.
[2] *Phil. Mag.* 1875, (4), **49**, 9.

Best[1] it is also manufactured by acting with chlorine on a solution of sodium carbonate or bicarbonate at temperatures not exceeding 35°, the reaction being probably

$$3Na_2CO_3 + 3Cl_2 = NaClO_3 + 5NaCl + 3CO_2.$$

This reaction is of interest as usually hypochlorites alone are formed at low temperatures by the action of chlorine on carbonates.

Sodium chlorate crystallises in combinations of the cube and tetrahedron showing also tetartohedral faces, and having a sp. gr. of 2·29, which become damp when kept for a long time. It is much more soluble in water than the potassium salt, 100 parts of water dissolving according to Kremers

At	0°	20°	40°	60°	80°	100°	120°
Parts of $NaClO_3$	81·9	99	123·5	147·1	175·6	232·6	333·3

It also dissolves readily in warm alcohol.

Sodium chlorate melts at 302° (Carnelley) and is chiefly then for the most part converted into sodium chloride and perchlorate with evolution of only a small quantity of oxygen (Schlössing). It is chiefly used in the manufacture of aniline black, its greater solubility making it more suitable for this purpose than the cheaper potassium salt.

Sodium Perchlorate, $NaClO_4$, is prepared by heating the chlorate or by neutralising perchloric acid with soda. It is very soluble in water, from which it crystallises at the ordinary temperature in long pointed plates containing one molecule of water, and at 50° in anhydrous rectangular prisms.[2]

Sodium and Sulphur.

88 *Sodium Sulphides.* These compounds are prepared in a similar manner to the corresponding potassium salts (*see* p. 240), which they closely resemble. Sodium sulphide is manufactured on the large scale and used in the manufacture of soluble soda-glass.

Sodium Hyposulphite, $Na_2S_2O_4$. This salt, the formation and

[1] *Journ. Soc. Chem. Ind.* 1895, 865. See also Grossmann, *Journ. Soc. Chem. Ind.* 1896, 158.

[2] Potilitzin, *Journ. Russ. Chem. Ges.* 1889, i. 258.

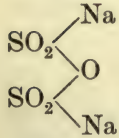
constitution of which have already been discussed (vol. i. p. 408) is used by the dyer and calico printer as a reducing agent for indigo, and is also employed in the laboratory for the purpose of estimating free oxygen or the quantity of that element contained in substances from which it is readily evolved.

Normal Sodium Sulphite, Na_2SO_3. The anhydrous salt is obtained as a crystalline precipitate by heating a cold saturated solution of the hydrated salt, and remains unaltered in the air. The hydrate $Na_2SO_3 + 7H_2O$, is prepared by saturating a solution of a known quantity of sodium carbonate with sulphur dioxide and then adding the same quantity of sodium carbonate. The crystals which are deposited are transparent monosymmetric prisms, which lose the whole of their water at 150°. The solution has an alkaline reaction and sharp taste. Crystals of the hydrate $Na_2SO_3 + 10H_2O$ are obtained, according to Muspratt, by allowing the aqueous solution to evaporate over sulphuric acid.

Sodium sulphite is used as an "antichlor" to remove any excess of chlorine from fabrics which have been bleached with chloride of lime, and sometimes also as an antiseptic.

Sodium Hydrogen Sulphite, $NaHSO_3$. If a solution of sodium carbonate is saturated whilst cold with sulphur dioxide, this salt separates out in cloudy crystals, and alcohol precipitates it from aqueous solution as a white powder. It has an acid reaction, smells of sulphurous acid, and has an unpleasant sulphurous taste. A saturated solution of this salt is a commercial article, and is used by brewers for sterilising their casks.

Sodium Disulphite or *Sodium Metabisulphite*, $Na_2S_2O_5$, or



is obtained by supersaturating a soda solution with sulphur dioxide, and may be prepared on the large scale by passing sulphur dioxide into dry monohydrated sodium carbonate,[1] $Na_2CO_3 + H_2O$. It is a white crystalline soluble salt which gradually evolves sulphur dioxide in the air and is converted into sodium sulphate.

89 *Normal Sodium Sulphate*, Na_2SO_4. This compound is com-

[1] Carey and Hurter, *Ber.* 1884, **17**, 33c.

monly known in the anhydrous state by the commercial name of *Salt-cake*, whilst the hydrate, $Na_2SO_4 + 10H_2O$, is called Glauber's salt. We find the first mention of this salt in Glauber's work *De naturâ salium*, published in 1658. He obtained it as the residue left in the preparation of hydrochloric acid by the action of oil of vitriol upon common salt, and believed this simple aperient to be possessed of most valuable medicinal properties, whence it came to be known as *Sal mirabile Glauberi*.

The salt occurs native in the anhydrous condition as thénardite, and in solution in sea-water and in the water of salt-lakes, as well as in large quantities in certain mineral springs. Thus the water at Friedrichshall contains large quantities of this salt, which since 1767 has been obtained by evaporation and used in medicine as *Sal aperitivum Fridericianum*. A native compound of sodium sulphate with calcium sulphate termed *glauberite* is also found in several localities.

Sodium sulphate is prepared on an enormous scale as salt-cake, the first step in the manufacture of carbonate of soda, by the Leblanc process, no less than 408,173 tons of salt having been converted into salt-cake during 1895, in the United Kingdom. For this purpose common salt is decomposed either by sulphuric acid or by the combined action of sulphur dioxide, air, and aqueous vapour. The details of these processes will be described under the head of the soda manufacture.

Sulphate of sodium is also obtained as a residue in many chemical operations, especially in the preparation of nitric acid from Chili saltpetre in the sulphuric acid manufacture.

If ordinary Glauber's salt be allowed to remain exposed to the air, or more quickly if heated, the anhydrous salt is obtained, and if a solution of Glauber's salt saturated at about 35° be slightly heated, rhombic crystals of the anhydrous salt separate out. These are identical in form with crystals of thénardite, and isomorphous with those of silver sulphate, Ag_2SO_4. It has a specific gravity of 2·655, melts at 863°, possesses a saline bitter taste, has a neutral reaction, and does not dissolve in alcohol. When heated on charcoal before the blowpipe, sodium sulphide is formed.

One hundred parts of water dissolve the following quantities of the salt calculated as anhydrous sodium sulphate :—

	At 0°	10°	20°	30°	34°	40°
Na_2SO_4	5·02	9·00	19·40	40·00	55·00	48·8

	At 50°	60°	70°	80°	90°	100°	103·5°
Na_2SO_4	46·7	45·3	44·4	43·7	43·1	42·5	42·2

The saturated solution boils at 103°·5. The abnormal solubility of this salt has already been discussed (p. 99).

Hydrated Sodium Sulphate. The deca-hydrate, $Na_2SO_4 + 10H_2O$, commonly known as Glauber's salt, crystallises from aqueous solution at the ordinary temperature in large colourless monosymmetric prisms (Fig. 23), which are isomorphous with chromate and selenate of sodium. These crystals effloresce on exposure to dry air, melt in their water of crystallisation at 33°, and lose the whole of it below 100°.

FIG. 23.

Glauber's salt readily forms supersaturated solutions. These crystallise suddenly, when a small crystal of the salt is thrown into the liquid, or when the solution is cooled down to −8°. This rapid solidification is accompanied by a considerable rise of temperature.

The Hepta-Hydrated Salt, $Na_2SO_4 + 7H_2O$, is deposited in hard, clear, rhombic crystals when a supersaturated solution of the deca-hydrate is allowed to cool below 12°, or when such a solution is covered with a layer of warm alcohol of specific gravity 0·835.

Sodium Hydrogen Sulphate, $NaHSO_4$. This salt, commonly known as bisulphate of soda, is obtained in large asymmetric prisms when equivalent quantities of sodium sulphate and sulphuric acid are dissolved in water and the solution evaporated at a temperature above 50°. Like the corresponding potassium salt it is decomposed by alcohol at once into sulphuric acid and the normal salt. A hydrated salt, $NaHSO_4 + H_2O$, is also known.

Sodium Disulphate, $Na_2S_2O_7$, is formed by heating sulphur trioxide together with common salt (Rosenstiel):—

$$2NaCl + 3SO_3 = Na_2S_2O_7 + SO_2Cl_2.$$

The same compound is formed by the gentle ignition of acid sodium sulphate. When more strongly heated, it yields sulphur trioxide and normal sulphate.

Sodium Thiosulphate, $Na_2S_2O_3+5H_2O$. This salt, discovered in 1799 by Chaussier, and still known by its old name of hyposulphite of soda, is prepared on the large scale for use as an antichlor in the paper manufacture, and as a solvent for the unaltered silver bromide in photography. It is obtained by boiling sulphur with soda-ley, and passing sulphur dioxide into the yellow solution until it is colourless, or by boiling sodium sulphite with sulphur. A cheaper process is to decompose the soluble calcium thiosulphate obtained by the oxidation of alkali-waste, either by means of sodium carbonate or sodium sulphate. The solution of sodium thiosulphate is drawn off from the carbonate or sulphate of calcium and evaporated down in iron pans.

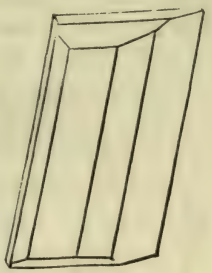


Fig. 24.

Sodium thiosulphate forms large transparent prisms belonging to the monosymmetric system, shown in Fig. 24. The salt is odourless, possesses a cooling taste, and does not possess an alkaline reaction, nor does it undergo alteration in the air. The crystals melt in their own water at 45°, and when heated to 215° all the water is driven off, whilst at 220° they decompose with separation of sulphur (Pape). The salt has a specific gravity of 1·672, is very soluble in water in which it readily forms supersaturated solutions, but does not dissolve in alcohol.

The aqueous solution cannot be preserved for any length of time without decomposition, as it very slowly deposits sulphur and is partially converted into sulphate. Sodium thiosulphate is represented by the formula $SO_2\begin{cases}ONa\\SNa.\end{cases}$[1] When treated with sodium amalgam it yields sodium sulphite and sodium sulphide :—

$$Na_2S_2O_3+Na_2=Na_2SO_3+Na_2S.$$

It is acted upon by iodine at the ordinary temperatures in aqueous solution with formation of sodium tetrathionate :—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

and is therefore employed in volumetric analysis in the estimation of iodine.

[1] Compare vol. i., p. 414.

Sodium and Nitrogen.

90 *Sodamide*, $NaNH_2$.—This compound, discovered by Gay-Lussac and Thénard, is prepared by passing dry ammonia gas over sodium heated to 300–400° in an iron retort, and forms a waxy mass of crystalline structure, which is white when pure but frequently has a greenish or olive-brown colour.[1] It softens at 149° and melts at 155°, and at a temperature of 500–600° slowly decomposes into its elements, but does not, as stated by Gay-Lussac and Thénard, yield a nitride of the formula Na_3N_2. When heated in a current of carbon dioxide sodamide glows with formation of caustic soda and cyanamide, and on warming with nitrous oxide it is converted into sodium azoimide:—

$$NaNH_2 + N_2O = NaN_3 + H_2O.$$

The water formed acts on a further molecule of sodamide forming caustic acid and ammonia.[3] *Sodium azoimide* is a crystalline substance readily soluble in water, and on treatment with acids yields azoimide N_3H (vol. i. p. 472.)

Sodium Nitrite, $NaNO_2$, is formed in a similar manner to the potassium salt, and is usually prepared by heating sodium nitrate alone or with iron filings, but then always contains a certain quantity of the nitrate and hydroxide; to obtain the pure salt silver nitrite is treated with the equivalent amount of a solution of sodium chloride. It crystallises in oblique four-sided prisms or transparent rhombohedra, is somewhat hygroscopic, and in solution is gradually oxidised by the oxygen of the air to sodium nitrate. It is largely used in the preparation of the coal-tar colours.

91 *Sodium Nitrate*, $NaNO_3$. This salt, commonly known as cubic saltpetre or Chili saltpetre, is of special historical interest as it was by the examination of differences in crystalline form exhibited by this compound and ordinary nitre that the distinction between the alkalis potash and soda was first observed by Bohn in 1683. Boyle, somewhat later, noticed that cubic saltpetre was formed in the preparation of aqua regia from common salt and nitric acid, and Stahl first pointed out the distinct

[1] Titherley, *Journ. Chem. Soc.* 1894, i. 504.
[2] See, however, Zehnder, *Ann. Phys. Chem.* 1894, **52**, 56.
[3] Wislicenus, *Ber.* 1892, **25**, 2084.

character of the alkali-basis of common salt, and fully described the preparation of cubic saltpetre.

Sodium nitrate occurs in nature as a wide-spread deposit known as "Caliche" in the rainless districts of South Peru and Bolivia. In these beds it is associated with common salt, gypsum, sodium sulphate, and smaller quantities of sodium iodate, the crude material containing from 27 to 65 per cent. of the pure salt. This is purified by solution and crystallisation. After refining, the salt contains about 97·7 per cent. of pure nitrate, 1·84 of sodium chloride, 0·35 of sodium sulphate, and 0·11 of water.

The best mode of separating out the last 2 per cent. of sodium chloride is to add to the boiling and saturated solution one-tenth of its weight of nitric acid, stir it until cool, and collect the precipitated nitrate, which may then be washed by a dilute acid and afterwards dried.

Fig. 25.

Sodium nitrate crystallises in obtuse rhombohedra,[1] whose interfacial terminal edge angle is 106° 36′ (Fig. 25), and is therefore isogonous with calcspar, but is no longer considered to be isomorphous with it (p. 25).

The specific gravity of the salt is 2·26. It melts without decomposition at 316–318° (Carnelley), and when ignited undergoes decomposition with evolution of oxygen, nitrogen, and nitrous fumes. It is very soluble in water, and deliquesces when exposed to moist air. 100 parts of water dissolve:

	At −6°	0°	10°	20°	40°	60°	80°	100°	111°
Parts	68·8	72·9	80·8	87·5	102	122	148	180	200

This salt also dissolves in dilute alcohol. 100 parts of spirit, containing 61·4 per cent. of alcohol, dissolve at 26° 21·2 parts of sodium nitrate. It does not deflagrate so violently as nitre with charcoal or other inflammable bodies, but it has sometimes been used for making blasting and other powders which are not required to fire quickly.

Sodium nitrate is used in considerable quantities for the manufacture of nitric and also of sulphuric acid, but by far the largest quantity is employed as a manure, as it readily yields up

[1] Sénarmont, *Compt. Rend.* 1854, **38**, 105.

its nitrogen to plants growing in soil where it is present. For this purpose it has now largely replaced the ammonium sulphate formerly employed. In 1860 the output of the crude nitrate from South America was over 60,000 tons, and has steadily increased from that date, being about 764,000 tons in 1888.

Sodium and Phosphorus.

92 *Sodium Hypophosphite,* $NaH_2PO_2+H_2O$.—This salt is obtained by adding sodium carbonate to a solution of calcium hypophosphite, and allowing the solution to evaporate in a vacuum. Pearly tabular crystals are deposited, which deliquesce on exposure to the air, and are easily soluble in absolute alcohol. It is now employed in medicine for the same purposes as phosphorus.

Sodium Phosphates.—These well-defined salts exhibit clearly the characteristic properties of phosphoric acid. From Graham's researches we first learnt that phosphoric acid exists in three modifications:

Orthophosphoric Acid.	Pyrophosphoric Acid.	Metaphosphoric Acid.
H_3PO	$H_4P_2O_7$	HPO_3

Each of these can be converted into either of the other compounds, and to each corresponds a series of salts, viz.:—tribasic orthophosphates, tetrabasic pyrophosphates, and monobasic metaphosphates. As the acids, so the salts of one series can be transformed into those of another series (vol. i. p. 590).

Sodium Orthophosphates.—As orthophosphoric is a tribasic acid, three sodium salts exist according as one, two, or three atoms of the hydrogen in the acid are replaced by metal:—

(1) Trisodium or normal sodium orthophosphate, $Na_3PO_4+12H_2O$.

(2) Hydrogen disodium orthophosphate, $Na_2HPO_4+12H_2O$.

(3) Dihydrogen sodium orthophosphate, $NaH_2PO_4+4H_2O$.

These all give yellow precipitates of trisilver phosphate Ag_3PO_4, when their solutions are brought into contact with silver nitrate.

Normal Sodium Orthophosphate, Na_3PO_4.—This salt, first de-

scribed by Thomson [1] as phospho-carbonate of soda, is prepared by adding at least half as much caustic soda as it already contains to a solution of the next salt, common phosphate of soda, and evaporating to the point of crystallisation. The hydrated salt crystallises out, the mother-liquid retaining excess of caustic soda. The crystals freed from the liquor, are rapidly dissolved in twice their weight of hot water, the liquid filtered, and then left to crystallise (Graham). The anhydrous salt may be obtained by fusing common phosphate of soda or pyrophosphate, with an excess of carbonate of soda. The pyrophosphate is not altered by boiling with caustic soda (Graham).

The crystals, which contain 12 molecules of water, form thin six-sided prisms, which do not change on exposure to air, and have a specific gravity of 1·618. They melt at 76°·7, and at 100° lose all but one molecule of water, which is given off at a red-heat. 100 parts of water at 15°·5 dissolve 19·6 parts of the salt.

Nitrate of silver produces a yellow precipitate of trisilver phosphate:

$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3.$$

Di-Sodium Hydrogen Orthophosphate, Na_2HPO_4.—This salt is the common phosphate of soda, which was first prepared from urine, and described in 1740 by Haupt under the name of *sal mirabile perlatum*. It was afterwards obtained by neutralising phosphoric acid with soda, and in 1787 was introduced as a medicine by Pearson. It occurs in the blood of animals, and especially in the urine of the carnivora. It is best prepared from bone phosphoric acid by adding sodium carbonate so long as effervescence occurs. The precipitated phosphates of calcium and magnesium are then filtered off, and the liquid boiled down and allowed to crystallise. The large transparent crystals which form are monosymmetric prisms (Fig. 26) containing 12 molecules

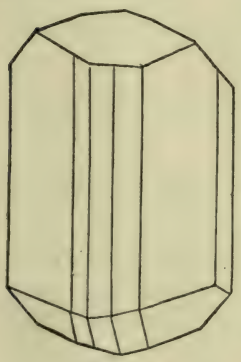


Fig. 26.

[1] *Ann. Phil.* 1825, **26**, 381.

of water of crystallisation. They have a specific gravity of 1·525, and melt at 35°, and are isomorphous with the corresponding sodium hydrogen arsenate $Na_2HAsO_4 + 12H_2O$. Exposed to air the crystals effloresce, but do not lose their form; and when dried over sulphuric acid at the ordinary temperature, or when gently heated to 45°, they lose all their water of crystallisation.

The following is the solubility of this salt in 100 parts of water:[1]

	At 0°	10°	20°	30°	40°	50°	60°	70°
Na_2HPO_4	2·5	3·9	9·3	24·1	63·9	82·5	91·6	95·0

80°	90°	99°
96·6	97·8	98·8.

The saturated solution freezes at − 0°·45, and boils at 105°.

This salt is insoluble in alcohol; it possesses a cooling saline taste, and turns red litmus solution blue. When brought into contact with nitrate of silver solution, a yellow precipitate of yellow trisilver phosphate is thrown down, and the solution becomes acid. It was supposed that this is due to the formation of free nitric acid, according to the equation:

$$3AgNO_3 + Na_2HPO_4 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

According to Ostwald, this does not, however, truly represent the reaction, which could not in any case be a complete one, as nitric acid dissolves silver phosphate. The following equation, probably, more nearly expresses the reaction:

$$3AgNO_3 + 2Na_2HPO_4 = Ag_3PO_4 + 3NaNO_3 + NaH_2PO_4$$

the presence of the sodium di-hydrogen phosphate causing the solution to show an acid reaction.

Common sodium phosphate is used as a mild purgative. The commercial salt frequently contains sodium sulphate as an impurity, which can be removed by recrystallising the phosphate from hot water.

Di-hydrogen Sodium Phosphate, NaH_2PO_4.—To prepare this salt phosphoric acid is added to a solution of common sodium phos-

[1] Mulder, *Scheidekund. Verhand.* 1864, 100.

phate, until the mixture no longer precipitates chloride of barium. It is then evaporated to small bulk, and allowed to stand for some days to crystallise (Mitscherlich). This salt is dimorphous, two kinds of large transparent crystals separating out, containing one molecule of water; according to Mitscherlich both are forms of the rhombic system, but according to Joly and Dufet, one of the varieties is monosymmetric.[1]

The crystals have an acid reaction, and a specific gravity of 2·04. They lose all their water of crystallisation at 100°, and at 204° lose one molecule of constitutional water (Graham) with formation of acid pyrophosphate:

$$2NaH_2PO_4 = Na_2H_2P_2O_7 + H_2O.$$

At 240° they give off the whole of their water and form monometaphosphate:

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

Di-hydrogen sodium phosphate is very soluble in water, but not in alcohol. Silver nitrate produces a yellow precipitate of trisilver phosphate, and two-thirds of the nitric acid is liberated:

$$NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3.$$

Sodium Pyrophosphates.—These salts are tetrabasic and give with silver nitrate a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$; they do not coagulate albumen, and their solutions when boiled with an acid yield the tribasic ortho-salts.

Normal Sodium Pyrophosphate, $Na_4P_2O_7 + 10H_2O$.—This salt is obtained in the anhydrous state as a colourless glassy mass by igniting the common sodium phosphate. When it is dissolved in water, and the solution evaporated, crystals of the decahydrate are deposited in monosymmetric prisms. The solution has an alkaline reaction. It is not converted into ortho-salt by boiling alone, but this conversion takes place rapidly on addition of an acid, even acetic, to the boiling solution (Stromeyer). When gently heated, or exposed over sulphuric acid in a vacuum, it loses all its water. 100 parts of water dissolve the decahydrate as follows:

At 0°	10°	20°	30°	40°	50°	60°	80°	100°
5·41	6·81	10·92	18·11	24·97	33·25	44·07	63·40	93·11

[1] *Compt. Rend.* 1886, **102**, 1391.

Di-hydrogen Sodium Pyrophosphate, $Na_2H_2P_2O_7$.—This salt is prepared by heating the common tribasic phosphate to 150° with strong hydrochloric acid, or by heating the tribasic di-hydrogen salt to a temperature of 190—204°, when it loses two molecules of water. It may also be prepared by dissolving the normal pyrophosphate in acetic acid, and precipitating the solution with alcohol; it is thus obtained as a white crystalline powder, which dissolves readily in water, the solution having an acid reaction.

93 *Sodium Metaphosphates.*—These salts, which were first discovered by Graham, exist in a large number of modifications, which all have the empirical formula, $NaPO_3$, but their molecular formula is in most cases some multiple of this. Some of them are insoluble in water, and the solutions of those which are soluble yield with silver nitrate a white gelatinous precipitate, whilst they are distinguished from the pyrophosphates by their power of coagulating albumen. They do not yield a precipitate with ammonium molybdate until they have been converted into an orthophosphate by boiling with nitric acid.

The most important of these salts, *Sodium Hexametaphosphate*, $(NaPO_3)_6$, often called deliquescent, vitreous, or Graham's metaphosphate, is prepared by heating to complete fusion either sodium di-hydrogen phosphate or microcosmic salt,[1] and also in a similar manner from all the other metaphosphates. The melted mass must be quickly cooled to avoid the formation of the dimetaphosphate. The product is a vitreous mass, which dissolves in water and alcohol, the solutions having a slightly acid reaction. It is unchanged even when boiled with caustic soda, but when treated with ammonium chloride yields a salt having the formula $Na(NH_4)_5(PO_3)_6$, and hence must be a hexametaphosphate. According to Tammann [2] it is a mixture of at least two isomeric hexametaphosphates.

Insoluble Sodium Metaphosphate, $(NaPO_3)_x$.—This salt whose molecular weight is unknown, but which is usually known as the *monometaphosphate*, is obtained by heating caustic soda with a slight excess of phosphoric acid,[3] or nitrate of sodium with syrupy phosphoric acid, and is a white powder almost insoluble

[1] Graham, *Phil. Trans.* 1833.
[2] *J. Pr. Chem.* 1892 (2), **45**, 467.
[3] Fleitmann, *Pogg. Ann.* 1849, **78**, 361.

in water, but soluble in dilute acids, and is converted by boiling caustic soda into sodium orthophosphate.[1]

Sodium Dimetaphosphate, $(NaPO_3)_2 + 2H_2O$.—This salt has hitherto been described as the trimetaphosphate, but has recently been shown to be the dimolecular compound by Tammann,[2] who has determined its molecular weight by Raoult's method; it is prepared by exposing microcosmic salt to a moderate heat (Graham), or by allowing the fused hexametaphosphate to cool slowly.[3] The cold solution in water is permanent and neutral, but on boiling it soon becomes acid with formation of sodium di-hydrogen phosphate.

Sodium Trimetaphosphate, $(NaPO_3)_3 + 3H_2O$. This is prepared by the action of a boiling solution of sodium sulphide on copper trimetaphosphate, which is obtained by fusing a mixture of phosphoric acid with a copper salt. It dissolves in 7·2 parts of water, and crystallises in slender needles. It has a strong tendency to form double salts.[4] It is usually described as the dimetaphosphate, but the determination of the molecular weight by Tammann has shown that it has the above formula.

In addition to these a large number of other metaphosphates have been described, namely, tetra-, penta-, octo-, deca-, and tetrakaideca-metaphosphates, having the general formulæ:

$$(M'PO_3)_4, (M'PO_3)_5, (M'PO_3)_8, (M'PO_3)_{10}, \text{ and } (M'PO_3)_{14}.$$

Sodium and Arsenic.

94 *Sodium Arsenates.*—These salts closely resemble the corresponding phosphates. An impure arsenate of sodium is prepared on the large scale by dissolving arsenic trioxide in caustic soda, and adding sodium nitrate; the solution is boiled down, and the residual mass heated in a furnace until it appears to be perfectly dry. This product is largely used in calico-printing as a substitute for cow-dung, which was formerly employed in clearing the cloth after mordanting. The mordant consists of a solution

[1] Maddrell, *Journ. Chem. Soc.* 1851, 373.
[2] *Zeit. Phys. Chem.* 1890, **6**, 122.
[3] Fleitmann and Henneberg, *Annalen*, 1848, **65**, 307.
[4] *Pogg. Ann.* 1849, **78**, 246.

of acetate of either aluminium or iron, and the cloth, after having been printed with these mordants, is hung up and exposed to air. In this, which is termed the *ageing process*, a portion of the acetic acid evaporates, leaving basic acetates of iron and aluminium firmly attached to the fibre of the cloth. A portion of these salts is, however, mixed up with the thickening or starch which must be added to the mordant in order that the impression shall be sharp. To remove this excess of unfixed mordant, the cloth is subjected to a peculiar treatment termed the *dunging process*. For this purpose it will not answer merely to wash the cloth in pure water, because the soluble portion of the mordant is then removed from the printed pattern, but attaches itself again to the unmordanted cloth, which it is intended should remain white. Long ago it was observed by the native dyers and calico-printers in India that if cow-dung be added to the washwater the excess of mordant can be removed without any staining of the cloth occurring. The action of the cow-dung in this process has not yet been satisfactorily explained, but experience has shown that sodium arsenate solution acts in a similar way, and at the present time the old process is generally superseded by the use of what is known in the trade as "dung substitute."

Sodium and Carbon.

95 *Sodium carbonate*, Na_2CO_3, commonly known as carbonate of soda or soda-ash, is prepared on an enormous scale, being the chief product of the alkali manufacture, which is described in detail below. The anhydrous salt is a white opaque porous mass or a white powder, which has a specific gravity of 2·5, melts at 1098° without decomposition in absence of moisture, and possesses an alkaline taste and reaction, but less strongly marked than those of potassium carbonate. When the anhydrous salt is brought in contact with water, heat is evolved owing probably to the formation of hydrates which then dissolve, forming an alkaline solution. Owing to the existence of several different hydrates the solubility of sodium carbonate shows an anomalous behaviour with rise of temperature, analogous to that of sodium sulphate (p. 99). 100 parts of water dissolve:

	At 0°	10°	20°	30°	32°
Na_2CO_3	7·1	12·6	21·4	38·1	46·4 parts.

From 34—79° the solubility remains constant at 46·2 parts and then decreases, the quantity dissolved at higher temperatures being as follows:

	80°	90°	100°	105°
Na_2CO_3	46·1	45·7	45·4	45·1.

A large number of different hydrates have been described, the most important of which are the *Decahydrate*, $Na_2CO_3 + 10H_2O$ and the *Monohydrate*, $Na_2CO_3 + H_2O$. The former is obtained when a hot fairly concentrated solution is allowed to cool, and forms large transparent monosymmetric crystals (Fig. 27), which are known commercially as *soda-crystals* or *washing soda*, and are manufactured on the large scale. They readily effloresce on exposure to the air, yielding the monohydrate as a white powder, which is also formed by heating the decahydrate to 34°, at which temperature it melts and loses nine molecules of water. The monohydrate crystallises in rectangular rhombic plates, and is prepared commercially and sold under the name of *crystal carbonate*. Both of these hydrates occur native, the former as *natron* and the latter as *thermonatrite*, in the soda lakes of Egypt and Hungary, and also at Vesuvius and Etna, and various parts of Asia, Africa and America.

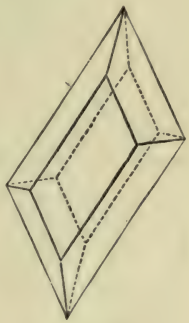


FIG. 27.

Of the remaining hydrates the *Heptahydrate*, $Na_2CO_3 + 7H_2O$, is the most important, and is obtained by allowing a warm saturated solution to cool in absence of air; it appears to be dimorphous, crystallising both in rhombohedra and rectangular rhombic plates.

Commercial anhydrous sodium carbonate prepared by the Leblanc process always contains sodium chloride and sulphate, as well as caustic soda and other impurities. That prepared by the ammonia soda process contains as a rule only sodium chloride as impurity. Soda crystals are usually much purer, and may be obtained perfectly free from impurity by repeated crystallisation.

Sodium Hydrogen Carbonate, $NaHCO_3$.—This salt, commonly known as bicarbonate of soda, is likewise prepared on the large scale. It occurs in commerce in the form of a white crys-

talline powder, or in crystalline crusts which consist of monosymmetric tables. It possesses a faint alkaline taste, and dissolves less readily in water than the normal salt. 100 parts of water dissolve at:

	0°	10°	20°	30°	40°	50°	60°	70°.
$NaHCO_3$	7·92	8·88	9·84	10·80	11·76	12·72	13·68	14·64.

A solution of the bicarbonate gives off carbon dioxide on boiling, and the solid salt decomposes on ignition into carbon dioxide, water and the normal salt:

$$2HNaCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Commercial bicarbonate of soda almost always contains some normal carbonate, and this may be removed by washing with small quantities of water; but, on drying, the residual salt is found again to contain some normal carbonate. A better method is to moisten the washed salt with alcohol, and then to dry it between folds of filter paper without application of heat. Even then it undergoes partial decomposition, and contains about one per cent. of the normal carbonate. In order to detect the presence of the latter salt in the bicarbonate, 1·0 gram of the salt under examination is mixed with 0·5 gram of mercurous chloride and 1·5 gram of water. This mixture is shaken in a stoppered bottle. If the normal salt be absent this mixture remains white for twenty-four hours; if this impurity be present, it becomes of a more or less grey tint.[1]

Trona, or *Urao*, is a carbonate of soda occurring native in Hungary, Egypt, Fezzan in Africa, India, and America. It is a compound of the normal with the bi-carbonate, and has the formula $Na_2CO_3 + 2NaHCO_3 + 3H_2O$. This is the body to which the ancients gave the name *nitrum*. It occurs in small monosymmetric crystals (Fig. 28), and it can be prepared artificially by boiling a solution of sodium bicarbonate and then allowing it to cool, when crystals of this salt separate.

Fig. 28.

[1] Hagen, *Zeit. Analyt. Chem.* 1870, **9**, 531.

THE ALKALI MANUFACTURE.

96 The history of the manufacture of carbonate of soda, or soda-ash, from common salt is one of peculiar interest. Previous to the year 1793 the whole of the carbonate of soda of commerce was obtained from the ashes of sea-plants, called varec or kelp, collected on the north-west coasts of France, Ireland and Scotland. The soda from this source was known as *barilla*. The quantity of alkali thus obtained from sea-plants was, however, much less than that which came to Western Europe from Russia and America in the form of potashes, the characteristic alkali of land-plants.

One of the first effects of the French Revolution was to cut off this supply of the latter alkali from France, and, therefore, to diminish important manufactures dependent upon its use. Under these circumstances the French Government of the day issued an appeal to the French chemists urging the importance of utilising all the materials deposited in their own country by nature, "so as to render vain the efforts and hatred of despots"; and commanding all citizens who "have commenced establishments or who have obtained patents for the manufacture of soda from common salt, to make known to the Convention the locality of these establishments, the quantity of soda supplied by them, and the quantity they can hereafter supply." A Commission was appointed to investigate this subject, and in 1794 they reported on thirteen different processes for the manufacture of soda-ash from common salt, the particulars of which had been submitted to them. The preference was given to the operations devised by an apothecary of the name of Leblanc, who had already erected a soda manufactory near Paris, which had been at work for some time previously. The report gives a full description of the various processes which constituted Leblanc's invention. These consisted of:—

(1) The salt-cake process, or the decomposition of common salt by means of sulphuric acid, and the consequent production of sulphate of soda, with evolution of hydrochloric acid gas.

(2) The black-ash process, or the decomposition of the sulphate of soda or salt-cake by means of chalk and coal, and the consequent production of black-ash, consisting essentially of

a mixture of soluble carbonate of soda (Na_2CO_3) and insoluble calcium monosulphide (CaS).

(3) The separation of the constituents of the last product by lixiviation with water and the preparation of the soluble carbonate of soda.

This process, elaborated by Leblanc before the French Revolution, is in fact that still largely employed in alkali-works, and, unlike most technical processes, has undergone no material alteration. The Commissioners say in their report:—"Citizens Leblanc, Dizé, and Shée were the first who submitted to us particulars of their process, and this was done with a noble devotion to the public good." Their establishment had been formed some time previously at Franciade; but the consequences of the French Revolution and of the war which followed having deprived them of funds, the works were suspended, and after the lapse of some time the manufactory became a national establishment and was successfully at work in the year 1794. The operations however did not proceed satisfactorily, the quantity of soda turned out was smaller than had been expected, the manufacture was discontinued, and Leblanc and his partners applied for and received assistance from the English Government. It is sad to have to relate that the man who thus originated a world-wide industry, and to whom we owe cheap soap and cheap glass, did not benefit from his discoveries, but died in a French asylum for paupers.

Other alkali works in France were more successful than Leblanc's original manufactory. Several of these were situated at Marseilles, the seat of the French soap trade, and conveniently placed for obtaining three of the necessary raw materials; (1) sulphur, imported from Sicily; (2) salt, obtained by the evaporation of salt-water by the sun's heat; (3) limestone;—it was however at the disadvantage of being at a distance from coal.

Although the process for making alkali was published in the *Annales de Chimie* for the year 1797, it is remarkable that seventeen years elapsed before this process was taken up in England by Mr. Losh. This may be partially accounted for by the fact that as war was then raging, communication between the two countries was almost entirely cut off, but was perhaps more especially due to the high war-duty on salt which existed up to the year 1823. The difference in cost of production is well shown by the fact that in 1814 soda crystals cost 60*l.* per

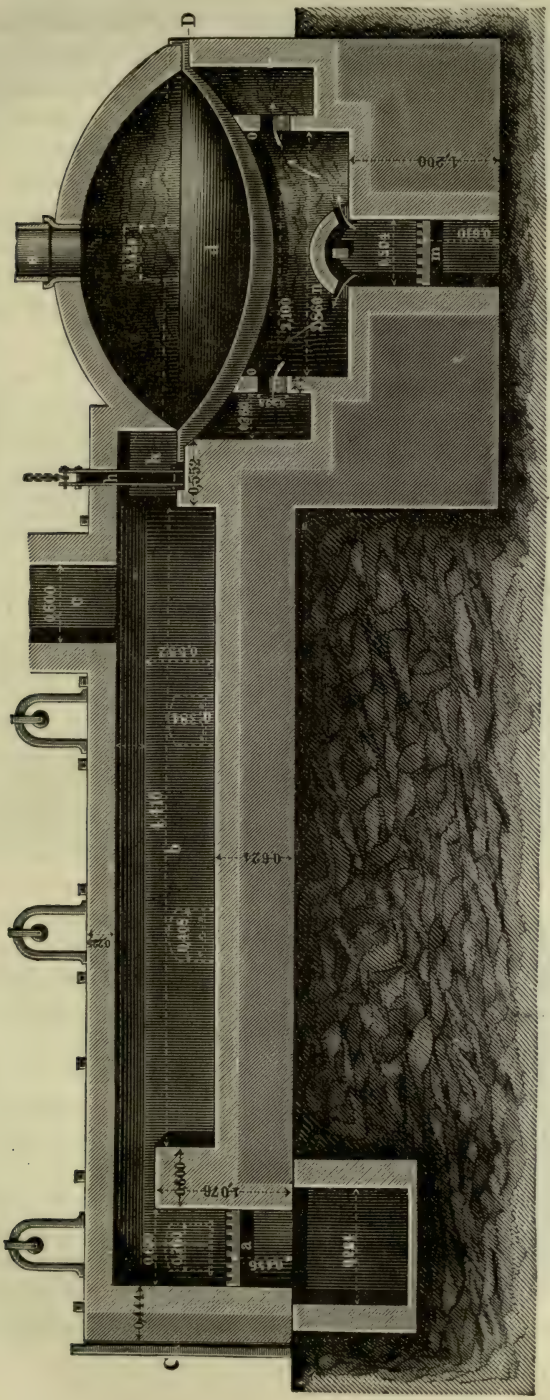


FIG. 29.

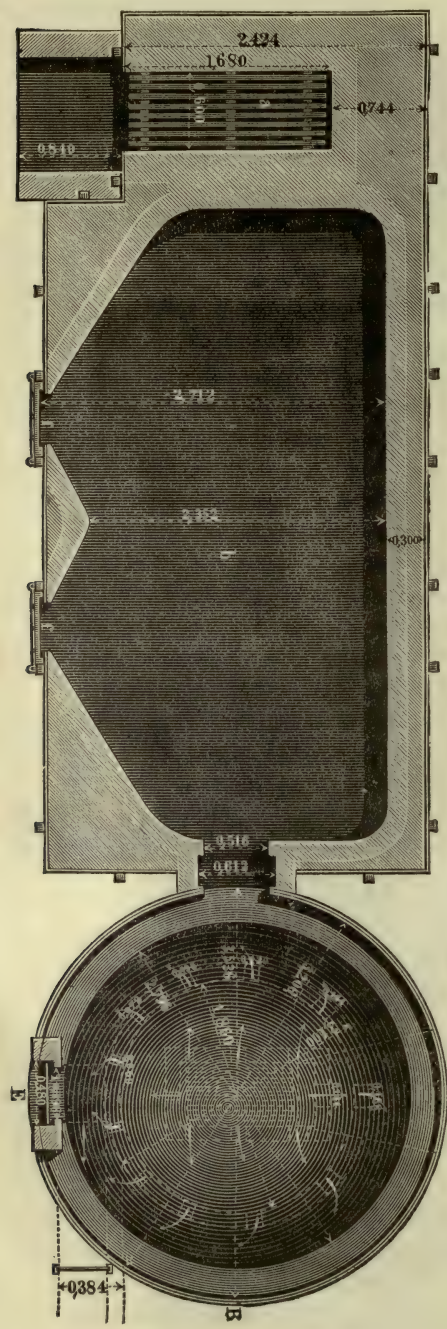


FIG. 30.

ton, whilst in 1896 the price of the same article was 2*l.* 15*s.* per ton.[1]

97 (1.) *The Salt-cake Process.*—This process is usually commenced in large cast-iron pots, and completed in reverberatory furnaces or roasters, shown in section in Fig. 29; in plan in Fig. 30; and in cross-section in Fig. 31. These consist of a large covered semi-circular iron pan built in the centre of the furnace and heated by a fire underneath, and of two roasters or reverberatory furnaces heated by fires placed one at each end, on the hearths of which furnaces the salt is completely decomposed.

The charge consists of 16 cwt. of common salt, which is placed in the iron pan, and on to this

[1] For full information as to the details of the alkali manufacture, see Lunge's *Sulphuric Acid and Alkali Manufacture* (3 vols.). 1894–6. Gurney and Jackson.

is run the quantity of sulphuric acid necessary completely to decompose it. This amounts to 123·5 gallons, or 1,800 lbs. of chamber acid having a specific gravity of 1·42. Torrents of hydrochloric acid are then given off, the decomposition which takes place being represented by the equation:

$$H_2SO_4 + NaCl = NaHSO_4 + HCl.$$

This process lasts about one hour, and the temperature of the mass rises to about 50°. All the hydrochloric acid which is thus

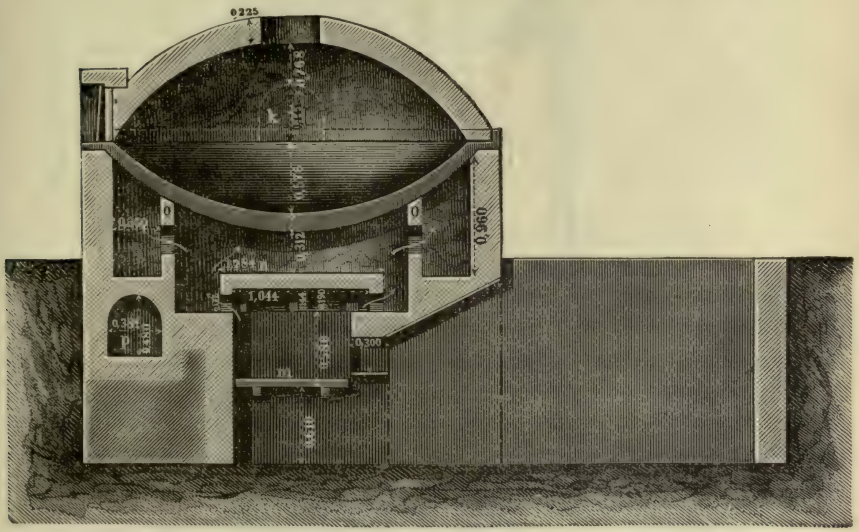


FIG. 31.

evolved passes directly from the pan into the hydrochloric acid condensing towers (Fig. 32). These towers are often 50 or 60 feet in height, and are usually built of Yorkshire flag clamped together with iron, the joints being rendered gas-tight by a cord of vulcanised rubber. The acid vapours enter the first tower direct from the salt-cake pan; and in passing up this tower, which is either filled with piled bricks or with hard coke, it meets with a descending current of water supplied from the cistern at the top. The strongly acid liquors flow away by a pipe at the bottom of the tower, and are stored by the manufacturer for subsequent use. Any hydrochloric acid vapours unabsorbed in the tower pass down a brick tunnel into the second tower, which they ascend and meet

another current of falling water. When the vapours reach the top of this tower they ought to be perfectly free from

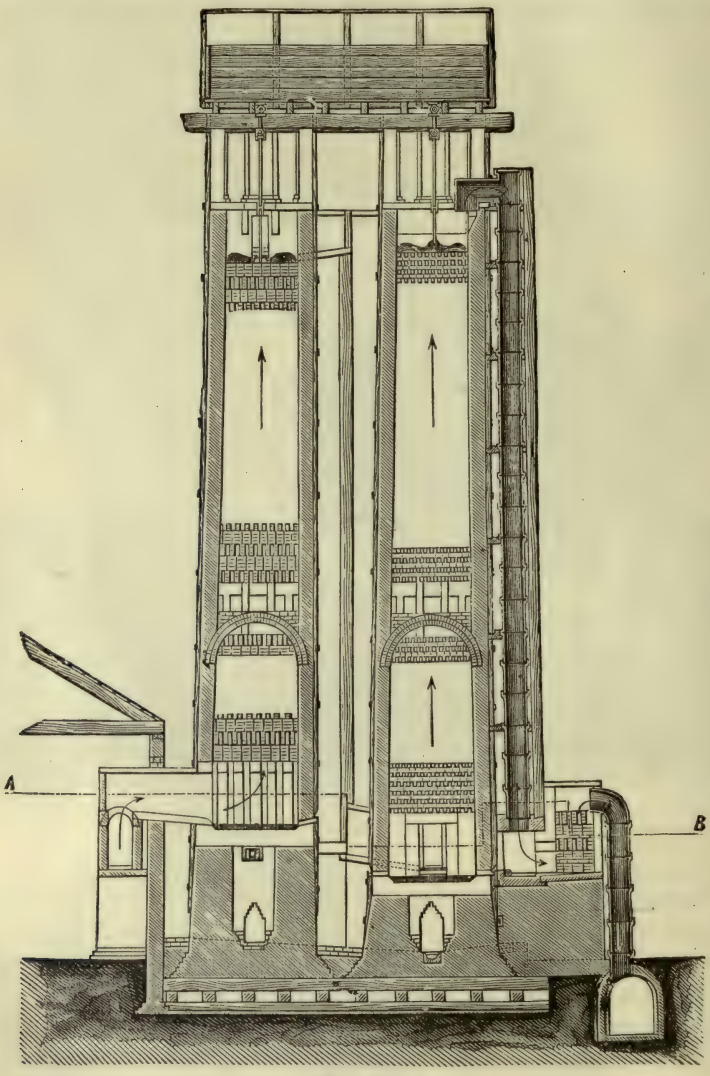


FIG. 32.

hydrochloric acid gas, and are then allowed to pass away into the chimney.

After the mixture has been heated for about an hour in the salt-cake pan and has become solid, it is raked on to the hearth

of one of the furnaces or roasters at each side of the decomposing pan. Here the hot air and flame from the fire at the end complete the decomposition into sodium sulphate and hydrochloric acid:

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

The acid vapours here evolved pass, together with the products of combustion of the fire, into the same condensers as the pan-acid, and there are all condensed to liquid. As soon as the decomposition is complete the salt-cake is withdrawn from the furnace and kept for the subsequent process. Ten of the above charges are usually drawn in one day, so that 8 tons of salt, and about the same weight of oil of vitriol, are used whilst nearly 5 tons of gaseous hydrochloric acid and nearly 10 tons of salt-cake are formed. The following is a complete analysis of an average sample of commercial salt-cake:—

Composition of Salt-cake.

Normal sodium sulphate	95·275
Hydrogen sodium sulphate	1·481
Sodium chloride	1·354
Calcium sulphate	0·923
Ferric oxide and insoluble matters ...	0·321
Water	0·187
	99·541

The furnaces just described are termed *open* roasters, in opposition to the second kind of salt-cake furnace, to which the name of *close* roasters is given. In the first kind all the acid vapours, both the concentrated acid from the pan and the roaster acid which is much diluted with air and products of combustion, pass into the same condenser. In this method of working it is difficult, therefore, to get a very strong acid, and much annoyance is caused by the condensers becoming choked with soot and dust from the fires.

Hence the second method is employed in many works. The pan, as shown in A, Fig. 33, is built at the side of the roaster instead of being placed in the centre, and the acid from the first part of the decomposition, being concentrated and

unmixed with air, passes by a long well-jointed earthenware

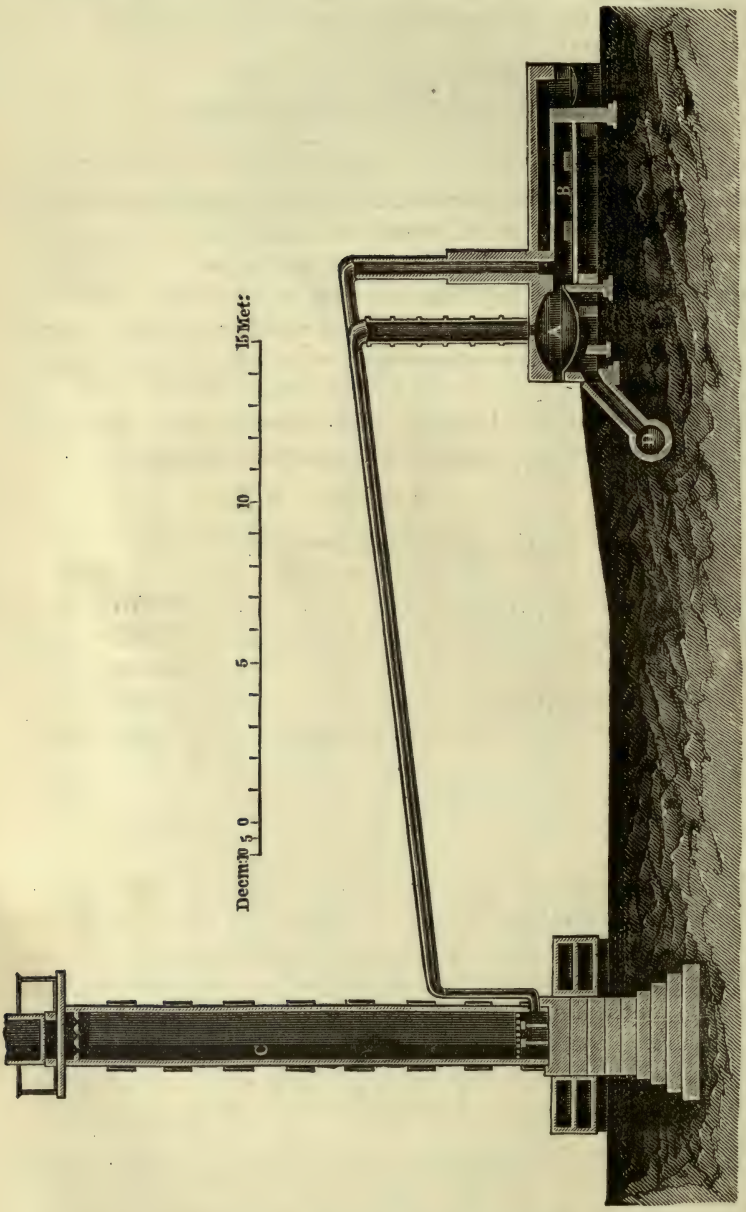


Fig. 33.

pipe into a condenser (c, Fig. 33), where a saturated or

fuming aqueous hydrochloric acid is prepared, whilst the gases from the roaster (B, Fig. 33) are separated from the products of combustion by inclosing the hearth of the furnace by a fire-brick arch, between which and the top of the furnace the flames and hot air from the fire pass. Thus the salt-cake is placed on the hearth of a kind of brick chamber or muffle (B), being simply heated by radiation from the hot arch at the other side of which the fire gases pass, so that no soot or dirt from the fire can be carried into the condensers, and these do not become clogged or choked, and thus a more perfect condensation is rendered possible; D shows the flue for carrying away the fire-gases from the pan and roaster. But unfortunately these advantages are not wholly unaccompanied by drawbacks, which, if not important for the manufacturer, are at least serious

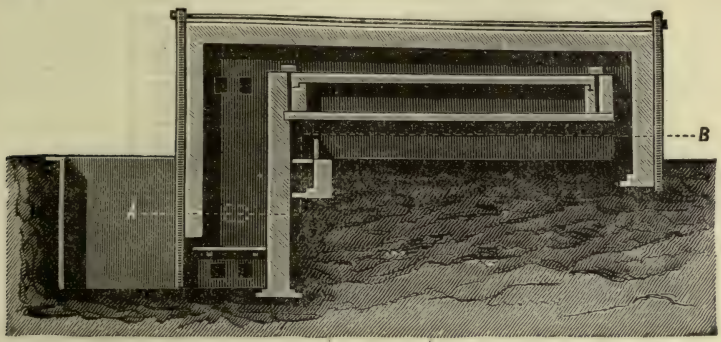


FIG. 34.

to his neighbours. The arch separating the roaster-hearth from the fire-gases cannot practically be kept gas-tight; it is continually cracking from unequal expansion, and as soon as a crack occurs, the hydrochloric acid gas is pulled or drawn by the draft of the chimney through the crack, and thus passes up the chimney where the pressure is somewhat less than that of the atmosphere, and is delivered into the air, rather than passing through the condensers, where the pressure is somewhat greater than the atmosphere. This is a fertile source of annoyance in the neighbourhood of alkali-works. Several suggestions have been made with a view of obviating this difficulty in the use of the closed roasters. One of the most feasible and ingenious of the proposed schemes is that patented by the late Mr. Deacon of Widnes. Figs. 34 and 35 show the construction of this furnace in section and in plan.

The fireplace is built contiguous to, but several feet below, the brick chamber or muffle in which the acid gas is evolved. It follows from this difference of level that there is a column of heated gases several feet in height immediately over the fire-bars, and the upward movement of this heated and rarefied air receives a check in going round the muffle, so that the ordinary state of things is reversed, and the pressure in the flue round the muffle is greater than that in the interior of the muffle, thus altogether preventing any chance of escape of the acid vapours from the muffle to the chimney, though allowing some of the gaseous products of combustion to pass through the unavoidable cracks into the interior of the muffle, but in such small quantity that they do not interfere at all with the successful working of the condensation. In Fig. 35, B shows the position of the salt-

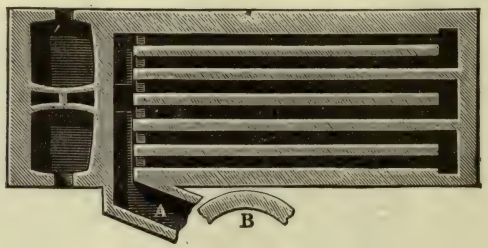


FIG. 35.

cake pot, and A is the flue carrying the products of combustion to the chimney.

Many attempts have been made to carry out the manufacture of salt-cake in mechanical furnaces, among which may be mentioned those of Jones and Walsh, Cammack and Walker, and Mactear.[1] The revolving furnace of the latter has been the most successful in practice, and consists of a circular revolving bed covered by a fixed arch, between which and the bed the furnace gases pass. The salt and acid are constantly fed into a large cup in the centre of the hearth where they mix and overflow into the outer portion of the circle, and are subjected to the action of the hot gases; by means of fixed stirrers the mass is continuously mixed and gradually worked to the circumference over which it then falls. The action is thus a continuous one and the amount of hydrochloric acid evolved is therefore constant, and in spite of the fact that it is mixed with the whole

[1] *Journ. Soc. Chem. Ind.* 1881, 29.

of the furnace gases, the condensation is carried out more readily and a more concentrated acid obtained than in the ordinary process, as in the latter hydrochloric acid is evolved at the beginning of the process in very large quantities, working the condensers to their maximum capacity, whilst for the rest of the time they are underworked.

Another important process for manufacturing salt-cake is that which from the name of the inventor is termed the *Hargreaves process*. The object of this is to manufacture salt-cake directly from salt, sulphur dioxide and water, so as altogether to dispense with the manufacture of sulphuric acid; and it depends upon the fact that, although sulphur dioxide cannot by itself decompose salt, it is able to do so in the presence of oxygen and water, if time enough be allowed. In order to effect this decomposition, a series of large kilns or stoves, built of brick, is so arranged that each kiln can be put into communication with its neighbour, and each heated by a fire. Each kiln is then filled with specially prepared cakes of dried and porous salt (NaCl), and the gases from the pyrites burners led directly into these kilns one after the other. By careful attention to temperature and to the quantity of air and steam admitted with the sulphur dioxide, it is possible in this way to decompose the salt into sulphate of soda (salt-cake) as perfectly as when heated by the old process with sulphuric acid. The chemical reaction is the same in both cases; hydrochloric acid gas is given off from the Hargreaves kilns as from the ordinary salt-cake pan or roaster and must in like manner be passed into the condensers:

$$4NaCl + 2SO_2 + 2H_2O + O_2 = 2Na_2SO_4 + 4HCl.$$

(For a comparison of the advantages and disadvantages of the two methods see Lunge, vol. ii. 2nd edition.)

98 (2.) *The Black-ash Process.*—The theory of this process is a simple one, so far as the chief products are concerned, but it is complicated when we come to consider the mode of formation of the many distinct compounds which make their appearance in the course of the reaction.

The first chemical change which the salt-cake (Na_2SO_4) undergoes in its passage to sodium carbonate is the reduction to sodium sulphide (Na_2S), by heating it with slack, or powdered coal; thus:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

The second change which occurs is the conversion of the sodium sulphide into sodium carbonate (carbonate of soda), by

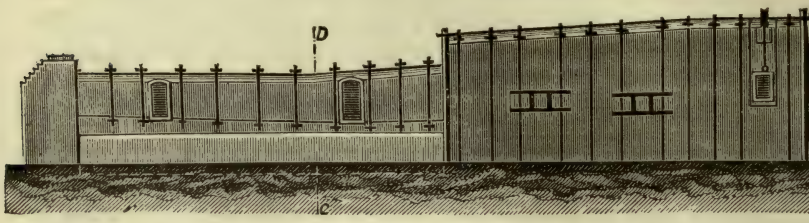


FIG. 36

heating it with chalk or limestone (calcium carbonate). The reaction which then takes place is represented by the equation :

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

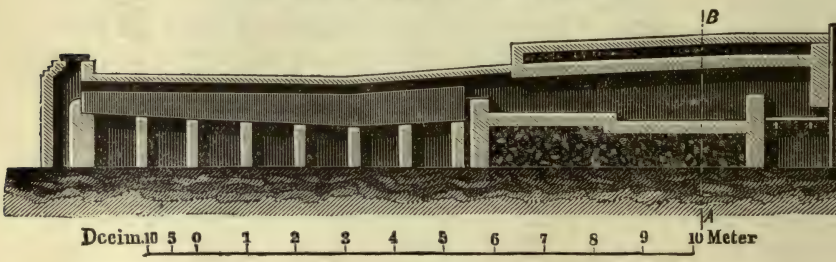
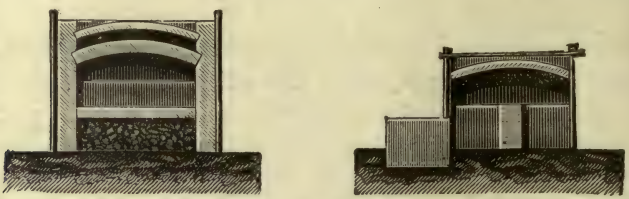


FIG. 37.

In practice these two reactions take place simultaneously. It is usually stated that the gas evolved in the first reaction



FIGS. 38 AND 39.

is carbonic oxide and not carbonic acid, but it has been shown by Kolb [1] and by Lunge and Fischer [2] that this is not the case.

[1] *Ann. Chim. Phys.* 1866 (4), **7**, 118.
[2] *Sulphuric Acid and Alkali*, 2.

Carbonic oxide is, however, formed at the end of the reaction, when the temperature is highest, by the action of carbon on the calcium carbonate present, the carbonic oxide escaping

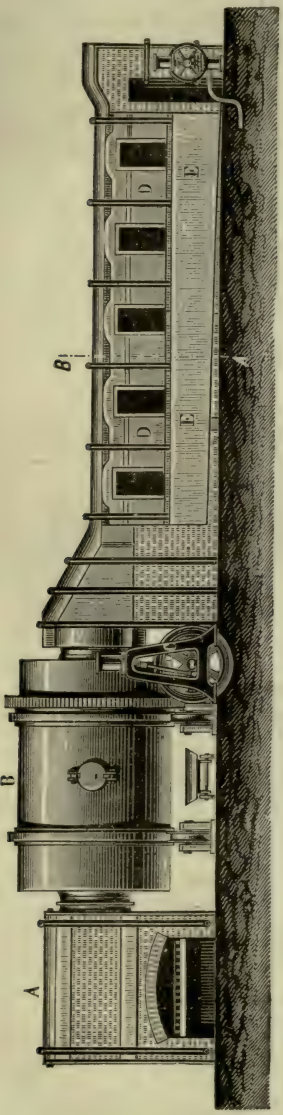


FIG. 40.

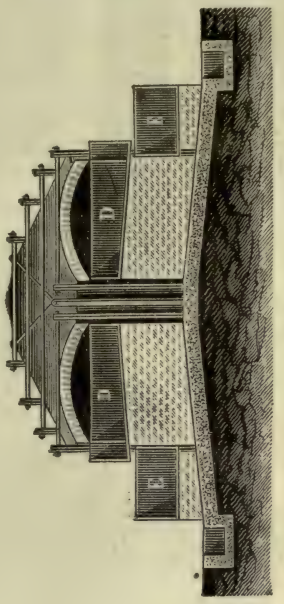


FIG. 42.

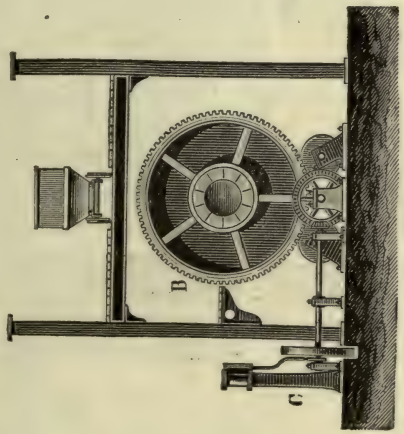


FIG. 41.

and burning with a yellow flame; the appearance of these flames, known as candles or pipes, shows that the reaction is nearly at an end. This reaction is also of importance for the

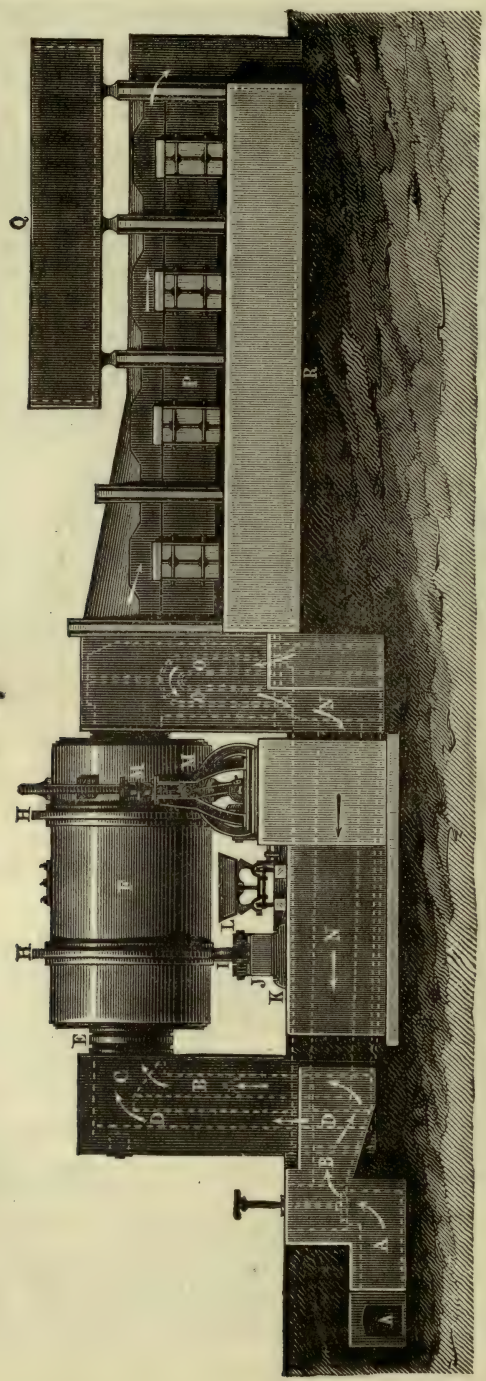


FIG. 43.

subsequent lixiviation of the product as it renders the mass porous, and the lime simultaneously formed has a similar effect inasmuch as in becoming hydrated it swells and breaks up the mass

In the actual manufacture, a mixture of about 10 parts by weight of salt-cake, 10 parts of limestone, and 5–7 parts of coal, is heated in a reverberatory furnace, termed a balling-furnace. Fig 36 shows the elevation, and Figs. 37, 38, and 39, show longitudinal and transverse sections of such a furnace. After exposure to the reducing flame of this furnace for two hours the charge, consisting of $4\frac{3}{4}$ cwt., is fluxed and fully decomposed, and then the liquid mass is scraped out into iron

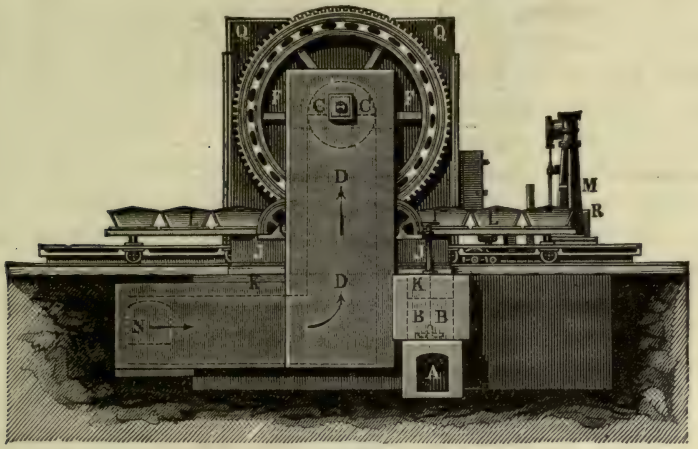


FIG. 44.

barrows or trucks and allowed to cool, and in this state is known, from the colour of the mass, as black-ash ball.

In place of the old black-ash furnace or balling-furnace in which the reaction is completed by hand-labour, a furnace, termed a revolving black-ash furnace, is now largely employed, the general arrangement of which is shown in Fig. 40. In this the mixing of the materials is effected mechanically. The charge, usually consisting of 30 cwt. of salt-cake, 32 of limestone, and 20 of slack, is introduced by means of a hopper into a large cylinder (B, Fig. 40), placed horizontally, through the axis of which flames from a furnace (A) are allowed to pass; this cylinder, worked by an engine (C, Fig. 41), revolves first at a slow rate and afterwards with an increasing and maximum velocity of

five or six revolutions per minute. The cylinder is from 10 to 12 feet in diameter, and from 15 to 18 feet long. Each charge takes about two hours to work off, and when completed a door in the side of the cylinder is opened and the fused mass allowed to flow into iron trucks placed beneath it. It yields 10 balls, each being a small truckful of black-ash, weighing 3 cwt. Another form of the black-ash revolver is shown in Figs. 43 and 44. In this arrangement the revolver (F) is fed with gas from a Siemens gas-furnace, and the regenerators (NN) for the recovery of the waste heat are placed below the revolver. It is questionable how far this plan of heating by gas can compete with the older method of heating by coal direct.

The advantages which the revolving black-ash furnace has over the hand-worked ones chiefly consist in the saving of labour and in the production of a material which possesses a more constant composition.

The following analyses of black-ash show that this substance contains a large number of other salts besides sodium carbonate and monosulphide of calcium, though these two constitute its main ingredients. In practice a large excess of limestone is used and this gives rise to caustic soda in the black-ash.

ANALYSES OF BLACK-ASH.

No. 1. Is the analysis of an English Black-ash by Kynaston.
No. 2. „ German „ Stohmann.
No. 3. „ French „ Kolb.

	1.	2.	3.
Sodium carbonate	36·88	44·41	44·79
Sodium sulphate	0·39	1·54	0·92
Sodium chloride	2·53	1·42	1·85
Sodium silicate	1·18	—	1·52
Sodium aluminate	0·69	—	1·44
Calcium sulphide	28·68	30·96	29·96
Lime	9·27	8·35	9·68
Calcium carbonate	3·31	3·20	5·92
Ferric oxide	2·66	1·75	1·21
Coal	7·00	5·32	1·20
Calcium sulphite	2·18	—	
Magnesia	0·25	0·10	
Magnesium silicate	—	—	
Alumina	1·13	0·79	
Water	0·22	—	1·51
Ferrous sulphide	0·37	—	
Silica	—	0·89	
Sand	0·90	2·20	
Ultramarine	0·96	—	
	98·60	100·93	100·00

99 (3.) *Lixiviation of the Black-ash.*—The next operation consists in the separation of the carbonate of soda from the insoluble calcium monosulphide, and the other impurities. This is easily effected by the process of *lixiviation*, or washing out the soluble sodium carbonate, leaving behind the monosulphide of calcium and the excess of lime and calcium carbonate as insoluble powders. In this process the object aimed at is to dissolve as large a quantity of the carbonate of soda with as small a quantity of water as possible. The arrangement of lixiviating vats for effecting this is the invention

of the late Mr. Shanks of St. Helens. A series of vats is employed in which the broken black-ash is placed; pure water is allowed to flow on to that portion of the ash which has already been nearly exhausted, and the solution then passes on until the nearly saturated liquors come in contact with the fresh black-ash. In this way the complete lixiviation of the black-ash is effected with the least quantity of water. The average time needed for working off a vat is about forty-eight hours. The residue remaining in the vats after the soluble matter has been extracted constitutes what is known as the alkali-maker's waste. This waste contains the whole of the sulphur from the salt-cake, and as a rule in the state of insoluble monosulphide of calcium. It was for a long time thrown away, being either made into heaps which are apt to become a nuisance in the neighbourhood of the alkali works, or carried out to sea, or otherwise made away with.

It is impossible, however, by this process of lixiviation completely to wash out the soluble carbonate of soda, so that we find about 3 per cent. of sodium left in the vat-waste, chiefly in the form of a sodium calcium carbonate $Na_2CO_3 + CaCO_3 + 5H_2O$.

A considerable excess of limestone is generally used in the manufacture of black-ash, and this, as already stated (p. 201), in the course of the reaction becomes converted into caustic lime; on treating the mass with water the caustic lime transforms a considerable quantity of the sodium carbonate into caustic soda, and calcium carbonate is formed:

$$Na_2CO_3 + CaO + H_2O = 2NaOH + CaCO_3.$$

Hence it happens that as a rule about one-third of the total amount of soluble soda present in the black-ash liquor is caustic. Besides this, the black-ash liquor usually contains small quantities of sulphide as well as ferrocyanide and thiocyanate of sodium. In order to separate the sulphide of sodium as well as the caustic soda which the black-ash liquors contain, these liquors are frequently carbonated or simultaneously oxidised and carbonated by allowing the liquid to fall down towers, filled with coke, up which in the first case carbonic acid, and in the second hot air in addition passes. In order to evaporate the black-ash liquors the waste heat of the black-ash furnace is employed. Large

pans, shown in D D, Figs. 40 and 42, are filled with the liquor, the water boiled off, and the crystals which are deposited scraped out into the drainers (E E, Figs. 40 and 42). These crystals are then heated, and yield common soda-ash. This common ash is further purified by exposure to heated air on the floor of a reverberatory- or refining-furnace. In this process any traces of the sulphides are oxidised to sulphates, the caustic alkali is carbonated, and the yellowish tint of the common ash, which is due to the presence of sulphide, is got rid of.

Alder Wright has made a series of experiments on the loss of sodium occurring in the black-ash process. He believes it to be as follows :—

Sodium sulphate undecomposed . .	3·49 per cent.
Sodium compounds rendered insoluble	5·44 „
Sodium compounds vaporised . . .	1·14 „
	10·07 „

100 *Alkali-maker's Waste.*—For every ton of soda ash produced from one and a half to two tons of waste are formed; and in the neighbourhood of alkali-works the latter accumulates in enormous quantities. It contains the whole of the sulphur burnt in the pyrites kilns, amounting to from 15 to 20 per cent. of its weight. The importance of recovering this sulphur not only for the sake of the manufacturers themselves, to whom it is otherwise entirely lost, but also for the sake of diminishing the nuisance to the neighbourhood, is obvious. The waste, even when carefully stamped down and when the surface is made as hard as possible or even covered with cinders, invariably undergoes oxidation; the insoluble monosulphide of calcium becomes converted into soluble compounds, and meeting with rain- or drainage-water dissolves, and the solution finds its way into the ordinary drains or streams of a district, and upon meeting with the carbonic acid of the air, or with the acid discharge from the alkali-works, evolves sulphuretted hydrogen sufficient to become a nuisance to the inhabitants of districts lying even several miles away from the waste. Many proposals have been made for recovering the sulphur from the waste. So far back as 1837 Gossage began a long investigation into this question, but failed to establish a process by which the sulphur could be profitably recovered. Schaffner in Germany, Mond in England, and

Mactear in Scotland, have devised processes which have been worked in certain localities, but were not sufficiently economical for general adoption. It is to the credit of Chance of Oldbury that by another process now generally used by alkali manufacturers, sulphur recovery from alkali-waste has been made remunerative, and the grave nuisance arising from the waste-heaps will in time be greatly diminished if not entirely removed. This process depends upon two reactions: the first of these is the decomposition of the alkali-waste by carbonic acid with formation of calcium carbonate and liberation of sulphuretted hydrogen; the second, the combustion of this gas in a current of air with production of sulphur and water. For carrying out the first of these reactions a patent was obtained by Schaffner and Helbig, whilst for the second a peculiar kiln invented by Claus is employed. For the proper working of both these reactions it is, however, necessary that the various currents of gases should be of regular and constant composition, and to attain this constancy a most ingenious plan of working is used by Chance. In the first place, in order that the stream of sulphuretted hydrogen should be constant, that of the carbonic acid needed to decompose the calcium sulphide must also not only be regular, but must not be diluted with atmospheric nitrogen to an injurious extent. These necessary conditions have been secured, so much of the atmospheric nitrogen which accompanies the carbonic acid generated from burning lime in kilns being eliminated as to render the remaining gases sufficiently rich in sulphuretted hydrogen to serve, not only for the production of sulphur by means of the Claus kiln, but also for the manufacture of sulphuric acid by burning the sulphuretted hydrogen, and allowing the sulphur dioxide and steam produced to pass into the leaden chambers. The apparatus by which this regular flow of the gases is secured and the sulphur obtained is of a somewhat complicated character. The principal features of the process consist in bringing a mixture of alkali-waste and water into a series of vessels connected by pipes, and furnished with inlet and outlet ways. Through these vessels lime-kiln gases, consisting almost entirely of carbonic acid and nitrogen, are passed, with the result that in the first vessel the carbonic acid is absorbed by the free lime present in the waste, with production of calcium carbonate, and by the calcium sulphide with production, in presence of water, of calcium carbonate and sulphuretted hydrogen. This gas passes on

to the second vessel, where it meets with fresh alkali-waste, and is absorbed with formation of calcium sulphhydrate, CaH_2S_2. Thus it will be seen that a twofold absorption takes place, first of the carbonic acid, and secondly of the sulphuretted hydrogen, so that in the last one of a series of vessels neither carbonic acid nor sulphuretted hydrogen escapes, whilst the inert nitrogen of the air is allowed to do so. When the gases issuing from one of the intermediate vessels contain a sufficiently large proportion of sulphuretted hydrogen evolved according to the decomposition:

$$CO_2 + CaH_2S_2 + H_2O = CaCO_3 + 2H_2S,$$

the outlet is opened, and the gases, rich in sulphuretted hydrogen and poor in inert nitrogen, are collected in a gasholder, to be used for making either sulphur or sulphuric acid. When the gases cease to be sufficiently rich in sulphuretted hydrogen the outlet is closed, and the gases passed into another one of the series of vessels containing fresh waste and water, and thus the first operation is repeated. By this means the decomposition of the waste is complete, the whole of the sulphur being withdrawn. The residue consists of precipitated carbonate of calcium, which is used either in the black-ash furnaces in place of limestone, or for the manufacture of cement.

Ammonia-Soda Process.

101 Of the numerous proposals which have been made to replace the Leblanc process for the production of carbonate, only one has proved commercially successful. This process depends on the well-known fact that when carbon dioxide is passed into a solution of sodium chloride containing ammonia a double decomposition occurs, and sodium bicarbonate and ammonium chloride are formed:

$$NH_3 + CO_2 + NaCl + H_2O = NaHCO_3 + NH_4Cl.$$

The bicarbonate being very slightly soluble in a solution of ammonium chloride, separates out and may be converted into soda-ash by calcining. The mother-liquors containing ammonium chloride are heated with lime or magnesia and the ammonia thus recovered; the only waste product is therefore calcium or magnesium chloride.

Simple as the process is from a chemical point of view, the

practical difficulties, chiefly of a mechanical nature, were so great, that although the process was patented in 1838 by Dyer and Hemming, it was first practically carried out in 1855 by Schloessing and Rolland near Paris. Even they did not succeed in entirely overcoming the numerous practical difficulties surrounding the subject, and the credit of having brought the process to an economical issue belongs to Solvay, who in 1861 established the ammonia-soda manufacture near Brussels, and from that time forward the proportion of soda manufactured by this process has steadily increased. In 1888 the quantity of soda-ash manufactured in the world was estimated at about 900,000 tons of which about 400,000 tons were manufactured by the ammonia-soda process, and in England, the chief home of the Leblanc manufacture, the amounts of salt decomposed in 1895 were 408,173 tons by the Leblanc process, and 428,614 tons by the ammonia-soda process.

The advantages of the ammonia-soda over the Leblanc process are that it yields a purer product at a less cost of manufacture, chiefly because of the use of the brine pumped directly from the salt beds, and gives rise to no noxious by-products. The proportion of sodium chloride lost is greater than in the Leblanc process as the reaction given above is never complete, and the undecomposed sodium chloride passes away with the calcium or magnesium chloride; great care has also to be exercised to avoid any considerable loss of ammonia, the cost of which is high, but these disadvantages are more than counterbalanced by the above-named advantages. On the other hand, in the ammonia-soda process the whole of the chlorine of the sodium chloride is lost, as no economical process has yet been devised of recovering it from the calcium or magnesium chlorides on a very large scale, notwithstanding numerous attempts, some of which have been partially successful. (See the Weldon-Pechiney process, vol. i. p. 159.) It is this fact which has hitherto enabled the Leblanc soda manufacturers to compete with the more recent process. This is of especial interest, inasmuch as the hydrochloric acid was at first regarded by the manufacturers simply as a nuisance, and its recovery was only brought about by the action of the Legislature; now it is in reality the staple product of the Leblanc manufacturers, and the soda must be regarded more or less in the light of a by-product. If at any time an economical method of recovering the chlorine in the ammonia-

soda process is discovered, there is little doubt that the older method of manufacture will quickly be completely superseded.

In carrying out the manufacture, a brine of specific gravity 1·196, previously freed from magnesium salts by the addition of a little milk of lime or of sodium carbonate, is saturated with ammonia in a suitable saturator. The apparatus patented by Solvay for this purpose in 1872 is shown in Fig. 45, and consists

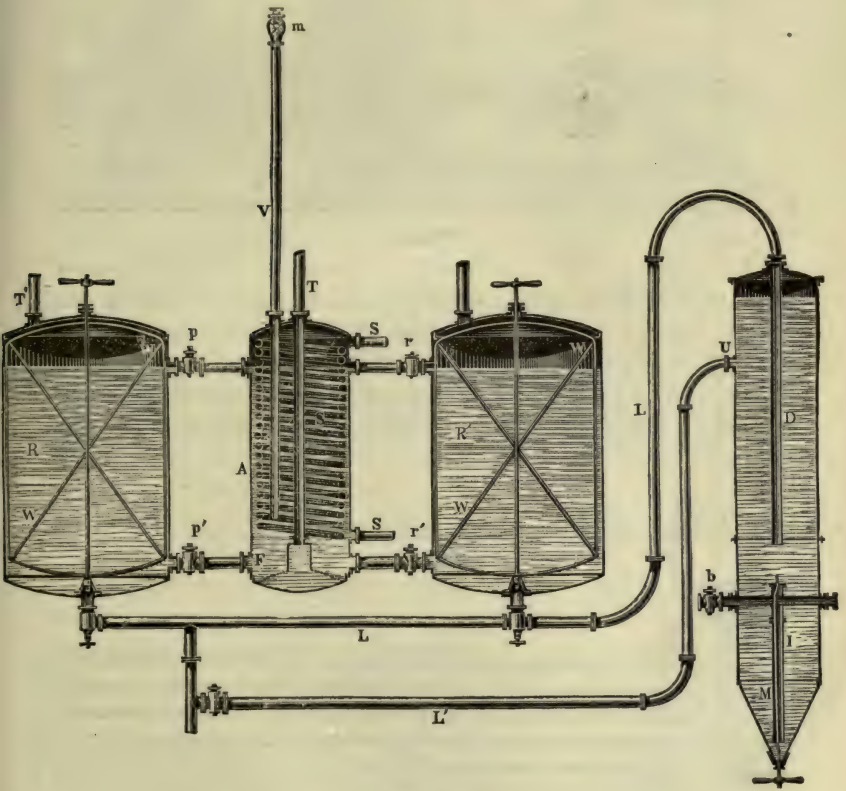


Fig. 45.

of two tanks R R′ for brine, and a cylinder A for dissolving the ammonia, which communicates with R and R′ above and below by the cocks p, p′, r, r.′ The tanks R R′ are connected alternately with A; supposing the one in connection to be R, the cocks p and p′ are opened, and ammonia gas obtained from the still passed into A by the pipe T, from which it is distributed by the perforated false bottom F and absorbed by the solution.

The brine in R, which has been mixed with a small quantity of milk of lime, is agitated by the stirrers W W′, and flows into A through one connection and back again through the other, the circulation being produced if necessary by the rapid revolution of the screw H (Fig. 46), inserted in one of the connecting pipes. The absorption of ammonia is attended by considerable

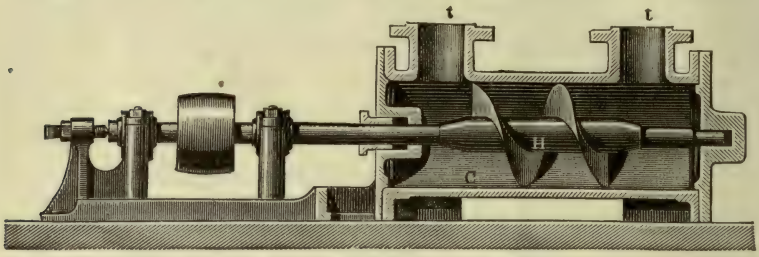


Fig. 46.

evolution of heat, and a cooling worm S, through which cold water circulates, is therefore placed in the dissolver A. The saturation is continued until the liquid has a specific gravity of 1·125, when the agitators are stopped, and the mud which settles run off by the mud-cocks at the bottom, or if there is a consider-

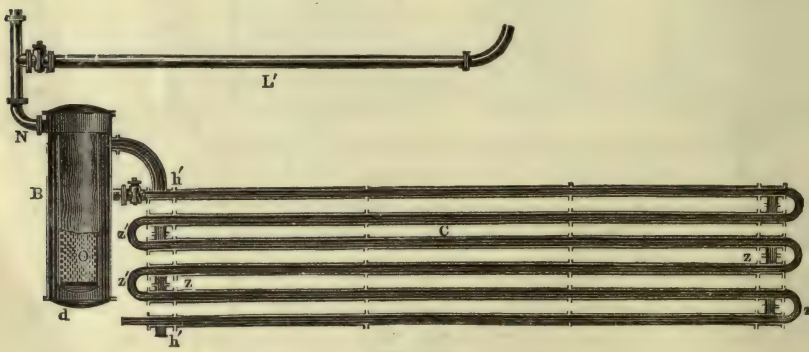


Fig. 47.

able quantity, the bottom liquor is run off through the decanting apparatus D. It is forced into the latter through the pipe L by allowing compressed carbon dioxide or air to act on the surface of the liquor in R, the mud falling to the conical bottom, from which it is removed by the scraper M, whilst the clarified liquor passes away by the overflow pipe U. To completely

remove suspended matter, this liquor and also such portions of the liquor in R as are nearly free from solids are forced through the cloth filter (Fig. 47), which consists of an outer cylinder B and a perforated inner cylinder O, the filter bag being either inside or outside the latter. The filtered liquor is next completely cooled by passing through cooling tubes C (Fig. 47) composed of concentric tubes, the liquor passing along the annular space between these whilst cold water is passed through the inner tubes.

The ammoniacal brine is now treated with carbon dioxide in the carbonating tower, shown in Fig. 48, which consists of a large number of superposed cylindrical compartments or drums, one of which is shown on a larger scale in Fig. 49. The bottom of each compartment has a large circular opening in the centre, over which is a perforated sieve having the shape of a spherical segment, which is supported by light stays and does not quite reach the inner wall of the drum. The ammoniacal brine enters some distance below the top of the tower by the pipe C and fills the tower nearly to the top, whilst the carbon dioxide, obtained partly from limekilns and partly from the calcination of the bicarbonate, is forced in at the bottom under a pressure of 1·5—2·5 atmospheres. It is divided by the sieve holes into numerous small streams which pass through the brine and reunite in the large central opening of the next, this being repeated in each compartment, so that

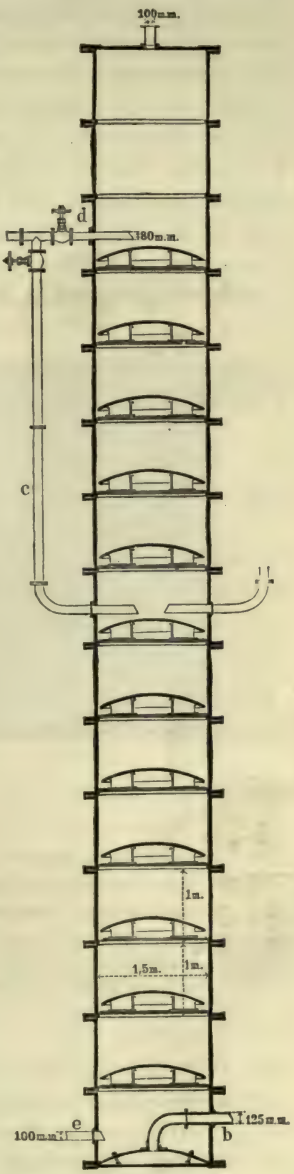


FIG. 48.

the liquor when it reaches the bottom of the tower is completely carbonated. The liquor is introduced some distance below the top of the tower and not at the top, as otherwise the escaping gases would carry away much free ammonia and thus impoverish the descending liquor.

This reaction also gives rise to considerable evolution of heat, and as the reaction is most complete at about 15°, cooling is necessary. This is partly effected by the expansion of the carbon dioxide as it ascends the tower, this being attended with absorption of heat, but the solution requires still further cooling, and this is brought about by allowing cold water to flow down the outside of the tower, or more satisfactorily by passing cold water

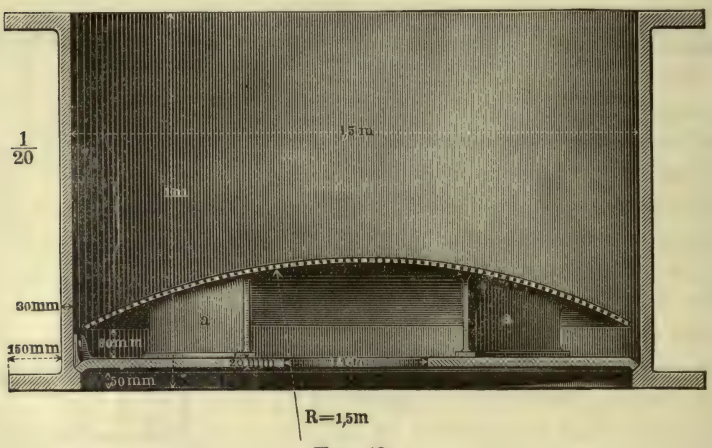


FIG. 49.

successively through a series of tubes in each compartment. The gas escaping from the top of the tower always contains ammonia, which is removed by washing first with brine and finally with sulphuric acid.

Every half hour a portion of the contents of the tower is drawn off from the bottom of the tower, and the pasty mass conveyed to vacuum filters, which retain the sodium bicarbonate, the filtrate consisting of a solution of ammonium chloride, together with some ammonium carbonate, sodium chloride and bicarbonate. The bicarbonate is sometimes washed with a little water, and is then calcined in revolving cast-iron furnaces, by which it is converted into sodium carbonate and carbon dioxide. As a rule the decomposition is not completed in this furnace,

but the ash is withdrawn when all ammonia has been driven off, at which stage it still contains about 25 per cent. of unaltered bicarbonate. The reaction is completed in a reverberatory-furnace, the ash being thus rendered more dense. The gases escaping from the calciner consist of ammonia, carbon dioxide, nitrogen and oxygen, and these are first cooled and then passed through a scrubber to remove ammonia, the remaining gas being then again used in the carbonating tower.

The mother-liquor from the sodium bicarbonate contains the greater part of the ammonia used in the process, which is recovered by heating with addition of lime or magnesia in an ammonia still similar in principle to that described under ammonium sulphate, the ammonia being then again used for saturating fresh brine. The spent liquor from the stills, consisting chiefly of a solution of calcium or magnesium chlorides, is as a rule, run to waste.

102 *Manufacture of Sodium Carbonate from Cryolite.*—Sodium carbonate is now also manufactured from cryolite, the double sodium aluminium fluoride $3NaF,AlF_3$, by a process devised by Thomsen,[1] which is founded on the fact that when the mineral is heated with chalk, carbon dioxide escapes, leaving behind a mixture of calcium fluoride and sodium aluminate:

$$2(3NaF,AlF_3) + 6CaCO_3 = 3Na_2O,Al_2O_3 + 6CaF_2 + 6CO_2.$$

The sodium aluminate is separated from calcium fluoride by lixiviation and the solution carbonated with carbon dioxide. A compound containing 45 per cent. of alumina, 20 per cent. of sodium carbonate, and 35 per cent. of water is thus precipitated in a granular state, from which the sodium carbonate is extracted by long continued washing with hot water.

A number of other proposals for the manufacture of soda have been made, for details of which reference may be made to Lunge's *Sulphuric Acid and Alkali*, 2nd edition, vol. iii.

Manufacture of Soda Crystals, Sodium Bicarbonate and Caustic Soda.

103 *Soda Crystals.*—For certain purposes, especially for household use, there is a considerable demand for the soda in the crystalline form containing 10 molecules of water. This is

[1] *Dingl. Polyt. Journ.* **166**, 441.

prepared by dissolving calcined soda-ash in hot water, allowing the impurities to settle, and then running the clear liquor into crystallising tanks. The monohydrated carbonate $Na_2CO_3 + H_2O$, known as "crystal carbonate," is also now manufactured on the large scale by Carey, Gaskell, and Hurter's process, in which the tank liquors are carbonated, freed from silica by the addition of bauxite, and from sodium ferrocyanide by passing through a superheater and thus raising its temperature to 180°; the liquor is then carefully evaporated to the requisite extent and yields a very pure crystalline product.

Manufacture of Sodium Bicarbonate. In the ammonia-soda process this salt is, as already mentioned, obtained as an intermediate product. The Leblanc manufacturers obtain it by exposing soda crystals enclosed in large chambers to the action of carbon dioxide generated by the action of hydrochloric acid on limestone. The gas is slowly absorbed by the crystals which lose their water of crystallisation and their transparency:

$$Na_2CO_3 + 10H_2O + CO_2 = 2NaHCO_3 + 9H_2O.$$

"Crystal carbonate" is now also employed in its manufacture, but special precautions must in this case be taken as the temperature is raised much higher by the reaction.

Caustic Soda is now manufactured on the large scale in the alkali works. For this purpose the red-liquors are used from which the black-ash crystals have been deposited. These mainly consist of a solution of sodium carbonate and caustic soda in varying proportions, but contain at the same time chloride, sulphate, cyanide, and sulphide of sodium as impurities. The red-liquors are first allowed to pass down a coke tower where they meet with a current of air, the sulphides being thus oxidised to sulphates. Then having been reduced to a specific gravity of 1·10 they are causticised by heating with milk of lime in large iron boat-pans or boilers. The clear caustic liquor is then run off, the lime-mud being well washed to extract the soluble caustic soda, and these washings used to dilute fresh quantities of the red-liquors. The dilute caustic liquors are then either boiled down in ordinary steam-boilers or in open pans, and afterwards concentrated in cast-iron flanged pots sufficiently large to hold from 8 to 10 tons of finished caustic soda, being often 9 feet in diameter and 5½ feet deep. These pans are built into brickwork, and are heated by means of a furnace placed either below or on one side. When the

temperature reaches 120° the liquor begins to boil, and ammonia gas is evolved from the decomposition of the cyanides. The temperature rises as the liquors become more concentrated, and as soon as it reaches 260° the pots are loosely covered and the fire then urged until the contents of the pot are raised to a dull red-heat. It is now necessary to oxidise the small quantities of sulphides and cyanides which are still contained in the caustic liquors. For this purpose either nitre is added from time to time, or air is pumped through the hot liquid. If nitre is used torrents of ammonia are evolved, and a black deposit of graphite resulting from the decomposition of the cyanides is formed. The white caustic soda thus prepared contains about 70 per cent. of Na_2O, or nearly 90 per cent. of the hydrate NaOH. A less concentrated product termed "cream caustic" is also made; this contains about 60 per cent. of Na_2O. When the operation of concentration is finished, the fused caustic is ladled out by means of copper ladles into iron drums, where it solidifies on cooling. In this way it can be transported to any distance without undergoing change.

Electrolytical Production of Caustic Soda.

Numerous attempts have been made to prepare caustic soda and chlorine simultaneously from sodium chloride by the electrolysis of its aqueous solution, which brings about the formation in the first instance of sodium and chlorine, the former then decomposing the water with production of caustic soda and hydrogen. The processes have failed usually on account of the formation of hypochlorite and chlorate by the union of the caustic soda and chlorine, which decreases the current efficiency, and also causes the rapid wearing away of the carbon used for the anode. The Castner process, which is radically different from previously suggested methods, is now successfully in operation at the works of the Castner-Kellner Company at Weston-point, as well as in Germany and America. The essential features of this process are the employment of a moving body of mercruy which completely separates the products of electrolysis, and by its movement takes the place of a diaphragm, the amalgam formed by the electric action being decomposed electrically as rapidly as it is so formed. The cell, which is divided into three compartments, is capable of being continuously rocked or

tilted, so as to give to the contained mercury a flowing motion from side to side. The two outside compartments contain the alkali chloride solution and the carbon anodes, while the middle compartment contains an iron cathode and the caustic solution. The solution of salt or chloride is continuously circulating through the outside compartments, wherein it is being electrolysed, and then returns to saturators where it is recharged with salt. The electric current traversing the salt solution liberates chlorine, and also forms sodium amalgam. The chlorine escapes from each cell through an aperture provided into one large connecting main, while the sodium amalgam, by the continuous back-and-forward tilting of the cell, passes to the centre compartment, where it acts as an anode during the passage of a current to the cathode, the sodium being acted on and going into solution as caustic. A regulated quantity of water is admitted hourly to the centre compartment of each cell, causing the pure solution of caustic to overflow through a discharge pipe into a large collecting pipe connecting with all the cells. Thus all the cells are connected with four mains, for the supply of saturated brine, for the return of the electrolytic solution to be resaturated, for collecting the chlorine, and for collecting the caustic. The cells are also electrically connected in series, and are capable of being cut out or put in operation at will. The current required is of low potential (4 volts), and the electrical efficiency very high, and as no hypochlorites are formed the wear of the carbon anodes is small. The caustic soda formed has a purity of 99·5 per cent. and the chlorine of 97 per cent., the remaining 3 per cent. consisting of hydrogen.[1]

104 *Sodium Cyanide*, NaCN.—This salt is obtained by neutralising hydrocyanic acid with soda, or by heating sodium ferrocyanide either alone or with metallic sodium:

$$Na_4Fe(CN)_6 = 4NaCN + FeC_2 + N_2$$
$$Na_4Fe(CN)_6 + 2Na = 6NaCN + Fe.$$

When obtained by passing hydrocyanic acid into alcoholic soda it is a white crystalline powder, which smells of hydrocyanic acid, and dissolves readily in water.

It is now manufactured on the large scale by Castner's method,[2] which consists in passing ammonia over metallic

[1] Castner, *Engineering*, September 28, 1894. Patents Nos. 16,046 (1892); 10,584 and 19,809 (1893).

[2] Patent No. 21,732 (1894).

sodium heated in an iron retort to 300–400°, yielding sodamide according to the equation:

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

This is then brought into contact with charcoal previously heated to dull redness, and thus converted into sodium cyanide and hydrogen:

$$NaNH_2 + C = NaCN + H_2.$$

The product is almost pure.

Sodium cyanide, like the potassium salt, is now very largely used for the extraction of metallic gold.

Silicates of Sodium.

105 Silica acts on sodium carbonate at high temperatures with evolution of carbon dioxide and formation of silicates, different silicates being obtained according to the time of heating, the temperature, and the relative proportions of the two substances taken. Unlike potassium, however (p. 263), sodium is capable of forming an *orthosilicate*, Na_4SiO_4, whilst the silicate richest in potassium is $K_8Si_3O_{10}$. If silica and sodium carbonate be fused together in equal molecular proportions, *sodium metasilicate*, Na_2SiO_3, is formed, and of this compound a number of definite crystalline hydrates have been obtained, crystallising with from 1 to 9 molecules of H_2O.

Soluble Soda Glass is obtained by heating together 180 parts of white sand, 100 of calcined soda-ash, and 3 of charcoal in a reverberatory-furnace and also by dissolving powdered flint in hot aqueous caustic soda under pressure. Like the corresponding potash glass it consists of a mixture of several silicates, the melting point being higher the greater the proportion of silica present. Prepared by the first method soluble soda glass forms a transparent glassy mass, sometimes colourless, but generally of a yellow, brown, or green colour, which when powdered readily dissolves in boiling water, forming a thick viscid liquid. When concentrated ammonia is added to the solution, a silicate having approximately the composition $Na_2Si_4O_9$ separates out,[1] and a hydrate of this silicate, containing $12H_2O$, is formed when precipitated silica is dissolved in boiling caustic soda and the filtrate evaporated down.[2]

[1] Heintz, *Jahresb.* 1871, 276. [2] Walker, *Quart. Journ. of Science*, **3**, 371.

Silicate of soda is employed in fixing fresco colours by the process of stereochromy. It is also employed as a cement in the manufacture of artificial stone. This is made by mixing the solution with sand and lime; it is likewise used as a cement for joining the broken surfaces of porcelain, stone, &c. Another purpose for which soluble glass is employed is as an addition to soap. The so-called silicated soap, first introduced by William Gossage, is now prepared in large quantities by adding a solution of this compound to the soap whilst settling.

Sodium Silico-fluoride, Na_2SiF_6, is prepared in a similar way to the potassium compound, and is very similar to this latter salt; 100 parts of water dissolve at 17°·5, 0·652 parts of the salt, and at 101°, 2·459 parts (Stolba).

Borates of Sodium.

106 *Sodium Orthoborate*, Na_3BO_3.—When boron trioxide is fused with excess of caustic soda, three molecules of water are expelled and the ortho-salt remains:—[1]

$$B_2O_3 + 6NaOH = 2Na_3BO_3 + 3H_2O.$$

This salt is very unstable, indeed it cannot exist in solution, for when dissolved in water it is tranformed into a hydrated metaborate.

Sodium Pyroborate, or Borax, $Na_2B_4O_7$.—The history of this the most important of the borates is lost in obscurity. It has already been stated under boron (vol. i. p. 641) that in the works of the Latin Geber the word borax or baurach occurs, but whether or not this indicated the substance which we now call by that name is a mere matter of speculation. Even up to the end of the seventeenth century nothing certain was known either as to the source or the composition of borax, which was used as a flux, and which was early brought into European markets by the Venetians. It was not until 1747 that an exact knowledge of its composition was arrived at, when Baron pointed out that borax consists of a compound of boric acid (then called sedative salt) and soda.

Before the discovery of the boric acid lagoons (vol. i. p. 651) the boric acid of commerce was obtained from Asiatic tincal,

[1] Bloxam, *Journ. Chem. Soc.* 1862, 143.

which is a crude decahydrate of borax, $Na_2B_4O_7 + 10H_2O$, and occurs native in Thibet. Since then tincal has been found in immense deposits in North America, these being generally the bottoms of lakes which have dried up more or less completely, and large quantities are now put into the market from this source, the crude product simply requiring recrystallisation.

A large proportion of the borax used in Europe is still made from Tuscan boric acid, which is fused with half its weight of soda-ash in a reverberatory-furnace, the product lixiviated with hot water, and the borax allowed to crystallise. In France the two substances are boiled together and the product allowed to crystallise. A further source of borax is the mineral *boronatro-calcite*, $Na_2B_4O_7 + 2CaB_4O_7 + 18H_2O$, termed in commerce borate of lime or "tiza," and found in the nitrate beds of South America, and in the massive condition in Nevada, which is finely divided and fused with the requisite proportion of soda-ash and sodium bicarbonate, the product being lixiviated and recrystallised.

Anhydrous Borax or Borax Glass is best obtained on the small scale by fusing 124 parts of crystallised boric acid with 53 parts of dry sodium carbonate. A transparent glass is thus obtained having a specific gravity of 2·367, which becomes opaque on exposure to air from absorption of water.

Fused borax glass dissolves many metallic oxides, which impart their peculiar colours to the glass, and it is therefore largely used in blowpipe analysis. It is readily soluble in water, but insoluble in alcohol. It forms two important hydrates.

Octohedral Borax, $Na_2B_4O_7 + 5H_2O$.—This salt is deposited when a supersaturated borax solution is allowed to evaporate spontaneously in a warm place. This solution is prepared by dissolving three parts of the decahydrate (common borax) in four parts of warm water. Another plan is to dissolve borax in boiling water until the specific gravity of the solution rises to 1·246, and then allow the solution to cool. The crystallisation of octohedral borax begins when the temperature reaches 79°, and continues until it sinks to 56°, after which common borax is deposited. The crystals are hard transparent regular octohedra, having a specific gravity of 1·815.

Common, or Prismatic Borax, $Na_2B_4O_7 + 10H_2O$.—Anhydrous borax when exposed to moist air absorbs ten molecules of water and forms this salt. The decahydrate is deposited from solutions at all temperatures below 56°, in the form of large transparent

monosymmetric prisms (Fig. 50), which have a specific gravity of 1·71. The crystalline form of natural borax is shown in Fig. 51. When heated in the air the crystals swell up, losing their water and forming a spongy mass called *borax usta*, or burnt borax.

The impurities usually found in commercial borax are sodium carbonate, traces of the sulphates and chlorides of the alkali metals, and salts of magnesium and calcium. Sometimes it is adulterated with alum and common salt. Pure borax gives no effervescence with acids, and dissolves in two parts of hot water. The solution is not rendered turbid on addition of alkali,

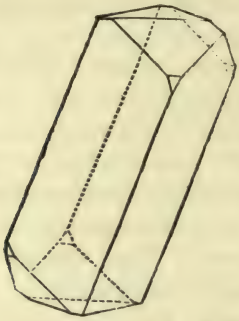


Fig. 50.

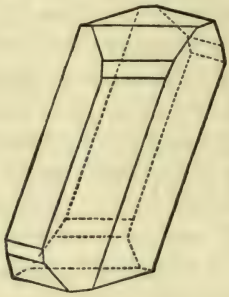


Fig. 51.

and does not give a precipitate either with barium chloride or silver nitrate. According to Poggiale,[1] 100 parts of water dissolve at—

0°	10°	20°	30°	40°	50°
2·83	4·65	7·88	11·90	17·90	27·41

60°	70°	80°	90°	100°
40·43	57·85	76·19	116·66	201·43

parts of $Na_2B_4O_7 + 10H_2O$.

Borax is largely used for a number of purposes, for glazing both earthenware and fabrics such as linen, as an antiseptic, and also in preparing clean surfaces of metals previous to soldering. The aqueous solution has an alkaline reaction, turning turmeric brown, and it is also alkaline to methyl orange; hence borax is often used for purposes which require a weak alkali.

Sodium Metaborate, $NaBO_2 + 4H_2O$.—This salt is formed

[1] *Ann. Chim. Phys.* 1843 (3), **8**, 467.

when borax is fused with the requisite quantity of sodium carbonate. It crystallises from water in monosymmetric crystals having the above composition.

Detection and Estimation of Sodium.

107 The presence of a sodium compound can be readily detected by the production of the yellow tint which it imparts to the non-luminous gas-flame. This reaction was first observed by Melville in 1752, and was made use of by Marggraf in 1759 to distinguish the base contained in common salt from that peculiar to the vegetable alkali which imparted a violet tint to flame.

The spectrum of the yellow soda flame consists of two bright yellow lines coincident with the two dark solar lines known as Fraunhofer's D-lines. These lines have a wave-length of 5896 and 5890 ten millionths of a millimetre, and lie so close together that in an ordinary one-prism spectroscope they appear as one line.

The spectrum-reaction of sodium is the most delicate one known, as has already been mentioned (p. 138).

The absorption-spectrum of sodium vapour has been mapped by Roscoe and Schuster.[1] A series of bands in the blue makes its appearance at a low temperature, and as this is raised bands in the red and yellow stretching as far as the D-lines come out. When the vapour of sodium is examined in a red-hot iron tube the colour of the limelight as seen through it is a dark blue.

In the processes of quantitative analysis sodium generally occurs together with potassium. The process for the separation of these two metals is described under that metal, as well as the indirect methods by which the quantity of the two metals can be ascertained (see p. 265). If it is desired to determine the sodium directly, the best process is the following one suggested by Bunsen. The alcoholic solution of the soluble double chloride of sodium and platinum is evaporated in a flask which is filled with hydrogen gas and reduced by exposure to light, or by addition of a reducing agent such as aldehyde. Sodium chloride, hydrochloric acid and metallic platinum are then formed; the solution of common

[1] *Proc. Roy. Soc.* 1874, **22**, 362.

salt is filtered from the platinum, evaporated to dryness, and the weight of the salt ascertained after gentle ignition. As sodium chloride is volatile at a red heat, it is advisable to transform the salt into sulphate before ignition.

The atomic weight of sodium has been most carefully determined by Stas. He found as the mean of ten experiments that 100 parts by weight of pure silver required from 54·206 to 54·209 parts of sodium chloride for complete precipitation. This gives a mean of 54·2075, hence the atomic weight of sodium is 22·87 (Ag = 107·13, Cl = 35·19).

POTASSIUM.

K = 38·85.

108 The discovery of this metal is described as follows by Davy.[1] "A small piece of pure potash which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4, in a state of intense activity; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. The whole apparatus was in the open atmosphere.

"Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash. I found that the platina was in no way connected with the result, except as the medium for exhibiting the electrical powers of decomposition, and a substance of the same kind was produced when pieces of

[1] *Phil. Trans.* 1808.

copper, silver, gold, plumbago, or even charcoal were employed for completing the circuit.

"The phenomenon was independent of the presence of air. I found that it took place when the alkali was in the vacuum of an exhausted receiver."

To this metal Davy gave the name of potassium. Soon after Davy's discovery, Gay-Lussac and Thénard[1] showed that the metal might be obtained in greater quantity by decomposing potash by means of metallic iron at a white heat. For this purpose iron turnings or wire were heated to whiteness in a gun-barrel covered with clay, and melted potash allowed to pass slowly over the ignited iron. The iron took up the oxygen of the hydrate, whilst potassium and hydrogen were set free. The potassium passed over in the state of vapour, and was condensed in a copper vessel containing naphtha. A still better method is that suggested by Curadau;[2] it consists in the decomposition of the potash by means of charcoal at a white heat.

Davy's discovery of the compound nature of the alkalis attracted universal attention, and chemists throughout Europe were occupied with a repetition of his experiments, and an examination of the remarkable properties of the singular metals which can thus be obtained. So singular indeed are these properties, that many chemists denied to these substances the name of metal, and by some they were considered to be compounds of hydrogen, this view being apparently borne out by the evolution of hydrogen when these metals are thrown into water. A more accurate examination, however, of the properties of these substances proved them to be of a truly metallic nature.

Sources of Potassium.—Potassium is found in nature, in a state of combination, widely distributed. It occurs as a constituent of many silicates, forming from 1·7 to 3·1 per cent. of the granite composing the earth's solid crust. Amongst the silicates which contain potash as an essential constituent, may be mentioned potash-felspar or orthoclase, leucite, and analcime. Pure chloride of potassium or *silvine*, KCl, is found in considerable deposits, together with *carnallite*, $KCl + MgCl_2 + 6H_2O$, in the neighbourhood of Stassfurt in Germany. This same salt and other potash compounds occur in small quantity in the water of the ocean, and in that of many lakes such as the Dead Sea, as

[1] *Ann. Chim.* **65**, 325. [2] *Ann. Chim.* **66**, 97.

well as in mineral waters and in ordinary spring water. Chloride of potassium is also found in cubic crystals surrounding the fumeroles of Vesuvius. All fruitful soil contains potassium compounds, derived from the gradual disintegration of the above-mentioned silicates. These are taken up by the rootlets of the plant, as no vegetable growth can flourish without this substance. It has been shown by Way that soil possesses the power of absorbing potash salts, whilst soda salts pass through it unabsorbed. The form in which the potash is contained in most soils is that of a salt of an organic acid; this becomes converted into carbonate by ignition. Potash is the essential alkali contained in the animal body, the soda salts being rapidly eliminated (Liebig).

The potash which sheep draw from the land is excreted in large quantity from the skin in the sweat, termed by the French *suint*. No less than one-third of the weight of raw merino wool consists of this material.

109 *Preparation of Metallic Potassium.*—The method first proposed by Curadau, and brought into a practical form by Brunner, has been much improved by Wöhler, and especially by Donny and Mareska.[1] This process depends upon the fact that at a white heat carbon reduces carbonate of potassium, as follows:

$$K_2CO_3 + 2C = 2K + 3CO.$$

An intimate mixture of charcoal and potassium carbonate is obtained by igniting crude tartar (acid potassium tartrate) in a covered iron crucible; the porous mass is rapidly cooled by dipping the crucible into cold water, and the charred mass introduced into an iron bottle. It has been usual to place the mixture in a wrought-iron mercury-bottle, connected with a copper receiver by a short iron tube, as shown in Fig. 52.

In the preparation of the metal potassium, according to Brunner's original method, serious explosions sometimes occurred, owing to the fact that at a very high temperature the metallic potassium unites with the carbon monoxide generated at the same time, to form a peculiar black compound, $K_6C_6O_6$, which is excessively explosive. By rapidly cooling the vapour of the potassium as it is produced, the formation of this compound may be prevented. This rapid cooling of the vapour is effected by using the condenser, first suggested

[1] *Ann. Chim. Phys.* 1852 (3), **35** 147.

by Mareska and Donny, shown in Fig. 53. It consists of two pieces of cast iron *d s*, which can be clamped together so as to form a shallow box about a quarter of an inch deep, ten to twelve inches long, and four to five inches in width. The socket at the one end fits on to the short tube placed in the neck of the bottle, or at the closed end of the retort, whilst the open end permits a free passage to the gases or vapours given off in the reaction. The object of this flattened condenser is to ensure the rapid cooling of the vapour of the metal, and thus prevent the formation of the explosive compound with carbon monoxide.

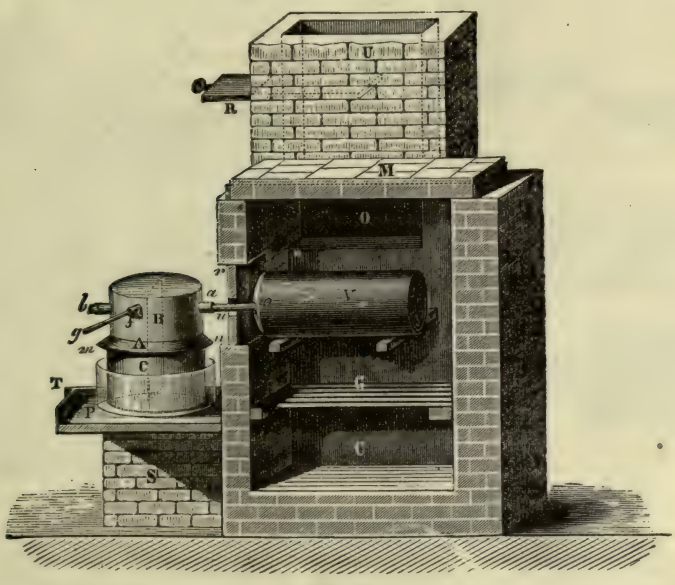


Fig. 52.

The above-mentioned reduction only takes place at a white heat, and hence it is necessary to prevent the oxidation of the iron or the retort by covering it with a coating of fire-clay. As soon as this temperature is reached the vapour of the metal begins to appear at the open end of the tube. The receiver is then adjusted to the end of the tube as shown in Fig. 54, and the metal begins to condense and drops out in the liquid state into a vessel filled with rock-oil placed beneath the receiver, which does not require to be artificially cooled. Should any deposit or obstruction occur in the tube, this must at once be removed by a

red-hot rod thrust into it. It is found in practice that about half the theoretical quantity of metal is obtained.

Potassium can be prepared on the small scale by the electrolysis of potassium cyanide. This salt is melted and then allowed to cool, so that a solid crust is formed; a current from three or four Bunsen's elements is then allowed to pass through the molten salt from poles made of gas carbon.[1]

A better method of obtaining potassium by electrolysis is that proposed by Matthiessen.[2] For this purpose a mixture of potassium chloride and calcium chloride in equal molecular proportions, which melts at a much lower temperature than the

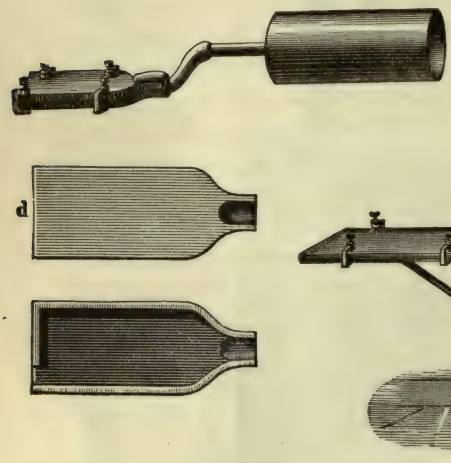


Fig. 53.

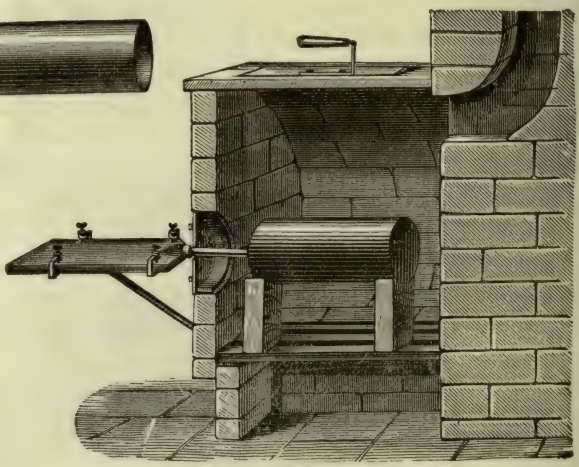


Fig. 54.

potassium chloride alone, is fused in a small porcelain crucible over a lamp, two carbon poles connected with six to eight Bunsen's elements being dipped into the fused salt. The flame of the lamp is then so adjusted that the portion of salt around the negative pole becomes solid, whilst around the positive pole the mixture is liquid, thus allowing the free escape of the chlorine. After the current has passed through for about twenty minutes in this way the crucible is allowed to cool, and opened under rock-oil, when a considerable quantity of pure potassium is found around the negative pole, no calcium being deposited.

[1] Linnemann, *J. pr. Chem.* 1858, **73**, 413.
[2] *Journ. Chem. Soc.* 1856, 30.

Potassium is also manufactured by the electrolysis of caustic potash by Castner's process, already described under sodium (p. 158), and by this method all danger of the formation of explosive compounds is avoided. There is however at present no great demand for metallic potassium, as the cheaper sodium is equally applicable for almost all purposes, and moreover, owing to the difference in their atomic weights, 23 parts of sodium are equivalent to 39 parts of potassium.

110 *Properties.*—Potassium is a silvery white lustrous metal with a bluish tinge, having a specific gravity of 0·875 at 13° (Baumhauer),[1] and it is therefore lighter than all other metals, with the single exception of lithium. It is brittle at 0° and possesses a crystalline fracture; at 15° it becomes soft like wax, and may be easily cut with a knife, and the two clean surfaces of the metal may be welded together like red-hot iron. It melts at 62°·5 (Bunsen), forming a liquid closely resembling mercury in its appearance. Potassium may be easily obtained in the crystalline form. For this purpose some of the metal is melted in a glass tube filled with coal-gas; as soon as the mass begins to solidify the tube is quickly turned round and the portion of metal still remaining liquid is poured off from the crystals; these form quadratic octahedra having a greenish-blue colour.[2]

Potassium boils at 667°[3], emitting a beautiful green-coloured vapour exhibiting a characteristic channelled-space absorption-spectrum (Roscoe and Schuster). The green colour of potassium vapour can be readily shown by evaporating a small portion of the metal contained in a wide glass tube three dcm. in length, through which a current of dry hydrogen gas is passed. On heating the metal, the tube becomes filled with splendid green-coloured vapour, condensing on the cooler parts of the tube in the form of a bright metallic mirror. When the hydrogen, which issues from the end of the tube, is lighted the flame is tinged with the characteristic violet colour of potassium. Next to cæsium and rubidium, potassium is the most electro-positive metal. In perfectly dry and pure air it does not undergo any change, but in ordinary air the clean surface of the metal soon becomes converted into caustic potash and potassium carbonate. The oxidation of a newly-cut surface of potassium is attended in the dark with luminosity (Baumhauer). Oxidation takes place so quickly when the metal is exposed to the air in thin

[1] *Ber.* 1873, **6**, 655. [2] C. E. Long, *Journ. Chem. Soc.* 1861, 122.
[3] Perman, *Journ. Chem. Soc.* 1889, i. 327.

layers, that sometimes ignition occurs, and the metal burns with its characteristic violet flame. When heated in the air to its point of volatilisation, it at once bursts into flame, but if the burning metal is plunged into perfectly dry air or oxygen the flame is immediately extinguished.

When thrown upon water potassium decomposes the water with great violence, sufficient heat being generated to ignite the hydrogen which is evolved, and which burns with the violet potassium flame. The molten globule swims about, being separated by a layer of steam from the surface of the water, and becomes gradually smaller, leaving at last a globule of fused potash, which causes an explosive burst as soon as its temperature sinks low enough to allow it to come actually in contact with the water.

Potassium acts as a powerful reducing agent, and hence it has been largely employed for the preparation of such substances as boron and silicon from their oxides, and magnesium, aluminium, and other metals from their chlorides. The cheaper metal, sodium, is now, however, generally used for this purpose. Potassium also decomposes nearly all gases which contain oxygen, and hence it is used in some cases to ascertain the composition of gases.

COMPOUNDS OF POTASSIUM

Potassium and Oxygen

Potassium forms only two well-defined oxides, namely, potassium monoxide K_2O and potassium peroxide K_2O_4. The first of these corresponds to the stable monovalent potassium salts and combines with water to form the hydroxide. The higher oxide does not yield corresponding salts, but behaves as a peroxide. In addition to these, oxides of the formulæ K_4O, K_8O_5, K_6O_4, K_4O_3 and K_2O_2 have been described, but their existence is doubtful.

Potassium Monoxide, K_2O. When the mixture of oxides obtained by burning potassium in slightly moist air, is strongly heated it loses oxygen and leaves a residue of the monoxide, which may also be prepared by heating caustic potash with potassium:—

$$2KOH + 2K = 2K_2O + H_2.$$

It is usually prepared by melting potassium and, without further application of heat, leading the requisite volume of pure and almost dry air over it.[1] According to Holt and Sims, the product always contains metallic potassium, and it is very doubtful whether the oxide has yet been prepared in a pure condition.[2]

The oxide obtained by these methods is a gray brittle mass, which has a conchoidal fracture, and is very deliquescent and caustic, combining with water with incandescence to form caustic potash.

Potassium Hydroxide, or Caustic Potash, KOH

111 This compound, generally known by its old name of caustic potash, was considered to be an oxide of potassium, but Darcet,[3] in the beginning of 1808, showed that ignited caustic alkali contains some other ingredient in addition to oxygen and the metal. He believed that this ingredient was in all probability water, inasmuch as the calculated quantity of alkali contained in the carbonate neutralises more acid than the same quantity of the ignited caustic alkali. From this time forward caustic potash was considered to be a compound of potassium oxide and water, and it was not until a much later period that it was recognised to be a *hydroxide*, or a compound which is derived from water by the replacement of a portion of the hydrogen by a metal.

In order to obtain caustic potash, the metal may be allowed to act on water, but it is generally prepared by decomposing a dilute solution of potassium carbonate with slaked lime. For this purpose one part by weight of potassium carbonate is dissolved in twelve parts of water, the solution placed in an iron or silver vessel provided with a lid, heated to the boiling point, and then milk of lime gradually added until a portion of the filtered liquid evolves no carbon dioxide when treated with an acid. The solution is allowed to settle, and the clear liquid drawn off into a well-stoppered vessel. This is then evaporated in a silver basin until the hydroxide begins to volatilise. In order to ensure the complete separation of the carbonic acid from the potash, not less water than that mentioned must be used, and the water which evaporates from time to time must be renewed, for

[1] Kühnemann, *Chem. Centr.* 1863, 491.
[2] *Journ. Chem. Soc.* 1894, i. 438.
[3] *Ann. Chim.* **68**, 175.

when only four parts of water are present to one part of potassium carbonate no decomposition takes place. A concentrated solution of caustic potash is found to decompose carbonate of calcium (Liebig). Commercial caustic potash is prepared in this way. It is usually cast in the form of sticks which contain more or less water as well as all the impurities of the original carbonate of potash, especially alumina, potassium chloride, potassium sulphate, and potassium silicate. It may be purified by dissolving in alcohol in the manner already described for caustic soda (p. 162).

Pure caustic potash may also be obtained by adding powdered potassium sulphate to a hot concentrated solution of barium hydroxide (baryta-water) until a small quantity of sulphate of potassium remains in excess; this is then removed by a careful addition of baryta-water. The clear solution poured off from the insoluble barium sulphate is finally evaporated in a silver basin, any baryta which remains in solution being deposited in the form of carbonate from contact with the carbonic acid of the air.[1]

Wöhler's process for obtaining pure caustic potash consists in decomposing pure potassium nitrate by metallic copper at a red heat. For this purpose one part of saltpetre and from two to three parts of thin copper foil are arranged in alternate thin layers in a covered copper crucible and exposed for several hours to a red heat. On cooling, the mass is treated with water, the liquid allowed to stand in a tall cylindrical stoppered vessel, and the clear liquid then evaporated as before.[2]

Properties.—Pure caustic potash is a hard white brittle substance, often exhibiting a fibrous structure, melting below a red heat to a clear oily liquid, and volatilising in the form of white vapours when more strongly ignited. The vapour of this substance decomposes, at a white heat, into potassium, hydrogen, and oxygen; this decomposition explains, according to Deville, the formation of potassium by Gay-Lussac's method.

Caustic potash rapidly absorbs carbonic acid and moisture from the air, and dissolves, with evolution of heat, in water. According to Bineau, one part of water dissolves 2·13 parts of caustic potash. When the concentrated aqueous solution is cooled, the hydrate $KOH + 2H_2O$ crystallises in transparent colourless acute rhombohedra. Crystalline hydrates, $2KOH + 9H_2O$ and $2KOH + 5H_2O$ have also been obtained.[3]

[1] Schubert, *J. pr. Chem.* 1842, **26**, 117.
[2] *Annalen*, 1853, **87**, 373.
[3] Göttig, *Ber.* 1887, **20**, 1094.

The aqueous solution of caustic potash, sometimes known as *potash lye*, possesses an acrid taste and a peculiar nauseous odour; it acts as a powerful cautery, quickly destroying both animal and vegetable substances. For this reason its solution cannot be filtered except through glass or sand, and it is best clarified by subsidence. The following table gives the specific gravity at 15° of solutions of potash of varying strength calculated by Gerlach [1] from the experiments of Tünnermann and Schiff:

Per cent. of KOH.	Specific gravity.	Per cent. of KOH.	Specific gravity.
1	1·009	40	1·411
5	1·041	45	1·475
10	1·083	50	1·539
15	1·128	55	1·604
20	1·177	60	1·667
25	1·230	65	1·729
30	1·288	70	1·790
35	1·349		

Caustic potash also readily dissolves in alcohol.

The *liquor potassæ* of the Pharmacopœia contains about 5 per cent. of the hydrate KOH, and has a specific gravity of 1·058. Caustic potash is largely used in the form of a lye for absorbing carbonic acid in both organic and inorganic analysis. It absorbs moisture very rapidly from the air, and may, therefore, be employed for drying certain gases and liquids, especially organic substances which do not dissolve it and are not acted upon by it. The chief commercial use, however, of caustic potash is for the manufacture of soft soap. The soap-maker formerly prepared his lye by lixiviation of wood-ashes; the solution thus obtained was causticised by boiling with milk of lime. At the present day the commercial carbonate is employed for this purpose.

Potassium Peroxide, K_2O_4

112 This oxide was discovered by Gay-Lussac and Thénard. It is best obtained by heating potassium in excess of slightly moist air or oxygen. The metal takes fire at a temperature of from 60° to 80°, and when the surface is kept clean, burns to peroxide. In order to obtain the oxide in the pure state, clean potassium

[1] *Zeit. Anal. Chem.* 1869, **8**, 279.

must be moderately heated, first in a current of dry air and then in dry oxygen. If the metal is at once exposed to oxygen, great heat is evolved and the glass is attacked. According to Vernon Harcourt,[1] it is best to bring clean dry potassium into a flask containing dry nitrogen, in which it is melted. The nitrogen gas is then gradually displaced by air; the gray film which covers the molten metal is seen to change to a deep blue; then a point is reached at which the rapid absorption of oxygen begins. Gradually, as the oxidation proceeds, the metallic coating of the inner surface of the bulb changes to a dead white; this, however, after a while assumes a yellow colour, due to the formation of the tetroxide.

Potassium tetroxide is a dark chrome-yellow coloured powder which fuses at a higher temperature than caustic potash, forming a black liquid which, when the temperature falls, forms crystals with shining tabular faces; at a white heat it is decomposed into potassium monoxide and oxygen. When exposed to moist air it loses oxygen, possibly forming potassium dioxide:[2]

$$K_2O_4 = K_2O_2 + O_2.$$

Thrown on to water it dissolves with considerable evolution of heat, forming caustic potash, hydrogen peroxide, and free oxygen. Carbon monoxide acts upon the peroxide at a temperature somewhat below 100° with the formation of potassium carbonate, a volume of oxygen equal to that of the carbon monoxide employed being liberated, thus:

$$K_2O_4 + CO = K_2CO_3 + O_2.$$

Phosphorus and sulphur act violently upon the peroxide with formation of potassium phosphate and sulphate. When metals such as potassium, arsenic, antimony, and zinc are heated with this compound, they are oxidised with evolution of light and heat, whilst several metals such as bismuth, lead, iron, and silver undergo oxidation without the phenomenon of incandescence.

Potassium and Hydrogen

113 *Potassium Hydride* $(K_2H)_x$.—Potassium, when heated to incipient redness in pure hydrogen gas, absorbs about one-fourth of the volume it would have evolved in contact with

[1] *Journ. Chem. Soc.* 1862, 267.

[2] Holt and Sims, *Journ. Chem. Soc.* 1894, i. 437.

water (Gay-Lussac and Thénard). A gray powder, possessing no metallic lustre and not melting below a red heat, is thus produced. The compound was further examined by Troost and Hautefeuille,[1] who found that when potassium is heated to 200° it slowly absorbs 126 vols. of hydrogen, whilst at 300–400° the absorption is rapid. The product is a brittle, lustrous substance resembling silver amalgam, and ignites spontaneously in the air. It is unaltered when melted in vacuo, but dissociates at 200°. In this compound, as in palladium hydride (vol. i., p. 137), hydrogen shows the properties of a metal in a marked manner.

Potassium and the Halogens

114 *Potassium Fluoride*, KF.—This is formed when aqueous hydrofluoric acid is neutralised in a platinum vessel with caustic potash or potassium carbonate, and the solution evaporated down. This salt crystallises in cubes. It is very deliquescent and has a sharp saline taste. When it is dissolved in aqueous hydrofluoric acid it forms an acid fluoride, KFHF, crystallising in quadratic tables. These melt when heated, and at a dark red heat decompose into potassium fluoride and hydrofluoric acid. Crystalline compounds, KF,2HF and KF,3HF, have also been obtained by Moissan.[2]

Potassium Chloride, KCl, is a substance closely resembling rock-salt. Indeed, in earlier times no distinction was drawn between these two compounds. It occurs in sea-water as well as in that of many mineral springs, and forms the chief portion of the Stassfurt potash-salt. This salt exists in a bed 20 to 30 meters in thickness, lying above the deposit of rock-salt, and consisting chiefly of polyhalite, $2CaSO_4, MgSO_4, K_2SO_4+2H_2O$; carnallite, $KCl,MgCl_2+6H_2O$; and kieserite, $MgSO_4+H_2O$, interspersed with layers or veins of tachydrite, $CaCl_2, 2MgCl_2+12H_2O$; boracite, $2Mg_3B_8O_{15}, MgCl_2$; kainite, $K_2SO_4, MgSO_4, MgCl_2+6H_2O$; and lastly sylvine, KCl. These last two appear to be formed by the action of water upon the preceding compounds. In these minerals a small quantity of the potassium chloride is replaced by potassium bromide, and crystals of anhydrite, $CaSO_4$, are found in the kieserite beds. The mine-

[1] *Ann. Chim. Phys.* 1874 (5), **2**, 273.
[2] *Compt. Rend.* 1888, **106**, 547.

rals composing this bed are all of them very deliquescent, and their position leads to the inference that the saline deposits at Stassfurt have been formed by the gradual evaporation of an inland sea or salt-water lake. This is rendered more probable by the fact that in the manufacture of sea-salt in the so-called salterns on the Mediterranean coasts similar salts are deposited from the mother-liquors. In addition to the deposits at Stassfurt, similar beds have been found at Kulusz, in the East Carpathians. These potash salts do not occur in the majority of saliferous beds, and this is probably due to the fact that the upper saline strata have in most cases been washed away, whereas in the Stassfurt deposit they have been protected by a water-tight stratum of clay.[1] The mode of manufacture of potassium chloride from these potash salts is identical with that proposed by Balard [2] and Merle [3] for the preparation of the chloride from sea-water, and by Hermann [4] for preparing it from certain mineral springs. These methods depend upon the fact that carnallite, which is more soluble in water than rock-salt or kieserite, is only formed in solutions containing an excess of chloride of magnesium, so that when the salt is dissolved in hot water and the solution cools, the double salt does not separate out, but the more soluble magnesium chloride remains in solution whilst a part of the chloride of potassium crystallises out. The crude carnallite is crushed and treated with water, or according to more recent practice with a mixture of the mother-liquors resulting from later processes of the manufacture, and steam passed in, the solution being usually kept under a slight pressure. After separation of the insoluble matter, the liquor is run into crystallising vessels and allowed to cool gradually, a large proportion of crude potassium chloride separating out. The mother-liquor is then concentrated, and on cooling yields a further deposit of the crude chloride. The crude potassium chloride is purified by washing first with washing liquor from a former operation, and finally with water, the impurities removed being sodium chloride and magnesium chloride and sulphate. The quantity of potassium chloride in the various commercial products is from 75 to 98 per cent.

A second method depends on the fact that carnallite is easily soluble in a hot solution of magnesium chloride, whereas sodium

[1] For a full account of these deposits, see Thorpe's *Dict. of Appl. Chem.* vol. iii. 265.

[2] *Jahresb. Chem. Technol.* 1865, 296.

[3] *Bull. Soc. Chim.* 1868, [2], **10**, 63.

[4] *J. pr. Chem.* 1853, **60**, 284.

chloride and magnesium sulphate are only slightly soluble in this liquid. The liquors drawn off from the latter salts deposit crystals of carnallite on cooling, which can be separated from the mother-liquor, and then dissolved in hot water; on cooling crystals of potassium chloride separate out, which only need to be washed with cold water in order to bring them up to 98—99 per cent. The different mother-liquors and wash-waters are again worked up for the preparation of the other salts which they contain.[1]

In the salines on the west and south coasts of France the mother-liquors remaining after the common salt has been deposited, having a specific gravity of 1·22, are preserved in reservoirs during the summer, when a mixture of magnesium sulphate and common salt (*sel mixte*) separates out. The mother-liquor from this is evaporated in flat pans and thus converted into carnallite, which is worked up as described.

Potassium chloride crystallises like sodium chloride, in cubes. It has a cooling saline taste; its specific gravity is 1·995; it melts at 800° and readily volatilises at a bright red heat; 100 parts of water dissolve 28 parts of potassium chloride at 0°, 32·7 parts at 15°, and 56·5 parts at 100°.

When potassium chloride is melted in a current of hydrogen gas, or when the fused salt is subjected to electrolysis, a dark blue mass is formed which contains a sub-chloride of potassium, the composition of which has not been satisfactorily ascertained.

Potassium chloride is used for the preparation of other potassium salts such as the chlorate, the carbonate, the chromate, the nitrate and potash alum, but by far the greatest quantity is used for the preparation of artificial manures, for which purpose the crude salt is employed.

Potassium Bromide, KBr.—When bromine is dissolved in caustic potash a mixture of bromide and bromate of potassium is formed. If this mixture be evaporated and gently ignited, the bromate is decomposed, and pure potassium bromide is left. The usual method of preparing the salt on the large scale is by the action of bromine and water on iron filings; the bromide of iron thus formed being then decomposed by potassium carbonate.

Potassium bromide crystallises in cubes possessing a sharp saline taste, is readily soluble in water, melts at 722° and volatilises at a high temperature. It serves as a valuable

[1] See *Ber. über Entwickl. Chem. Industrie*, **1**, 351.

medicine, especially in cases of nervous diseases. It unites with bromine forming a very unstable tribromide KBr_3.

Potassium Iodide, KI.—This salt is prepared in a similar way to the bromide. It crystallises like the two former salts, in cubes, which possess a sharp taste, and are very soluble in water. Potassium iodide melts at 685° (Meyer, Riddle, and Lamb), and can be easily vaporised at a higher temperature, the vapour having a normal density. 100 parts of water dissolve at 0° 127·8, and at 118°·4, the boiling point of a saturated solution, 222·6 parts of the salt, whilst at intermediate temperatures the solubility increases proportionally to the increase of temperature (Mulder). Potassium iodide is sparingly soluble in absolute alcohol. The commercial iodide of potassium generally possesses an alkaline reaction; in order to obtain it perfectly neutral it must be dissolved in the smallest quantity of water, neutralised with dilute sulphuric acid, the potassium sulphate precipitated by the addition of pure alcohol, and the solution allowed to crystallise (Groves). Potassium iodide is largely used in medicine both for internal and for external application, especially in scrofulous and syphilitic diseases.

Potassium Tri-iodide, KI_3.—This compound is formed by saturating a concentrated solution of potassium iodide with iodine. A brown liquid having a metallic lustre is obtained, and this on evaporation over sulphuric acid yields needle-shaped almost black crystals which possess a metallic lustre. They are very deliquescent, melt at 45°, and are decomposed at 100° into iodine and potassium iodide (Johnson).[1]

Potassium Iodotetrachloride, $KICl_4$, was prepared by Filhol in 1839, by the action of chlorine on a solution of potassium chloride containing iodine. It forms lustrous golden yellow crystals.

115 *Potassium Hypochlorite*, KOCl.—When chlorine is passed into a dilute cold solution of caustic potash or potassium carbonate a mixture of potassium chloride and potassium hypochlorite is obtained. This substance was first prepared by Berthollet, and the solution, known by the name "Eau de Javelle," was formerly largely used for bleaching purposes (see vol. i. p. 315). Pure potassium hypochlorite has not yet been prepared.

Potassium Chlorate, $KClO_3$.—It appears likely that this salt was known to Glauber. In one of his works he mentions that he is acquainted with a means of converting muriatic acid into

[1] *Journ. Chem. Soc.* 1877, i. 249.

nitric acid, and in his "Continuatio Miraculi Mundi" he mentions a peculiar kind of saltpetre which he had prepared by means of common salt. This was probably chlorate of potash. In like manner Winterl, in 1789, believed that he had converted muriatic acid into nitric acid by strongly heating muriate of lime (calcium chloride) in a retort with black oxide of manganese and leading the product into a receiver containing a small quantity of caustic potash. Higgins also stated in 1786 that by the action of dephlogisticated muriatic acid (chlorine) on the alkalis, a peculiar kind of saltpetre is formed.

About the same time Berthollet was employed in his classical investigation of the action of oxygenated muriatic acid (chlorine) on the alkalis, and in 1786 he discovered potassium chlorate, which he, according to the prevailing views, termed hyper-oxy-muriate of potash. He obtained it by the action of chlorine upon caustic potash, and he observed at the same time that a large quantity of muriate of potash (potassium chloride) was formed; thus:

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

Potassium chlorate was in fact formerly produced on the large scale by this reaction by passing chlorine into a hot concentrated solution of caustic potash or potassium carbonate. The crystals of potassium chlorate, being only slightly soluble in water, separate out when the solution is cooled, whilst potassium chloride remains in solution. In this reaction only one-sixth of the potash is obtained in the form of chlorate, the rest being transformed into the much less valuable chloride. In order to avoid this loss an indirect method of manufacture is now employed, chlorine being passed into hot milk of lime, which it converts into a mixture of calcium chloride and chlorate:

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

A quantity of potassium chloride exactly equivalent to the calcium chlorate present is then added, when the sparingly soluble potassium chlorate is formed together with calcium chloride, and crystallises out from the solution:

$$Ca(ClO_3)_2 + 2KCl = 2KClO_3 + CaCl_2.$$

By this means the whole of the potassium employed is converted into chlorate and the loss due to the formation of chlorides only affects the cheaper lime.

In practice chlorine is passed into milk of lime of specific gravity 1·04 until the liquid is nearly saturated. The clear solution is evaporated until it has a specific gravity of 1·18, potassium chloride is then added, and the whole boiled down until a specific gravity 1·28 is attained. On cooling potassium chlorate separates out, and a further quantity of the latter is obtained by cooling the mother-liquors in a freezing apparatus.

Potassium chlorate crystallises in large transparent monosymmetric tables (Fig. 55) which have a glassy lustre and which when they are of certain dimensions exhibit magnificent iridescent colours and emit light when rubbed in the dark. The crystals of potassium chlorate have a feebly acid and cooling taste similar to that of nitre. They melt without decomposition at 359°, and at 372° they begin to decompose with evolution of oxygen. The nature of the decomposition and the effect of the addition of certain oxides has already been discussed (vol. i. p. 217). 100 parts of water dissolve at 0° 3·3 parts, and at 104°·8, the boiling point of the saturated solution, 60·2 parts of the salt (Gay-Lussac).

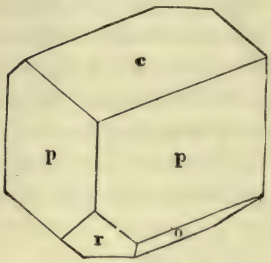


Fig. 55.

Potassium chlorate is used largely for the preparation of oxygen gas. It also acts as a powerful oxidising agent and is used in the manufacture of lucifer matches and for pyrotechnic purposes. It is largely employed in calico-printing and in the chemical laboratory. In large doses it acts as an irritant poison like nitre and other soluble potassium salts. It was formerly given in small doses in cases of scarlet fever, scurvy, and other diseases, as it was believed to act as an oxidising agent on the blood, but it has been shown that the whole of the salt passes out undecomposed in the urine. It is still employed for the purpose of allaying inflammation of the throat.

The powerful oxidising properties of potassium chlorate can be readily exhibited. If a small quantity of the powdered salt be thrown on to glowing charcoal a rapid combustion takes place. If a few grains of this salt, together with a few grains of flowers of sulphur are rubbed together in a mortar, loud explosions occur, and if a grain of the mixture be struck with a hammer a loud detonation takes place. Only very small

quantities of the mixture must be used, as otherwise the explosions may become dangerous. Further, if a small quantity of amorphous phosphorus be carefully mixed by means of a feather with the same quantity of powdered potassium chlorate, the mixture will explode when struck even a slight blow with a glass rod. This may also be shown by allowing a few drops of a solution of phosphorus in carbon bisulphide to fall on powdered potassium chlorate; after a few moments a violent explosion occurs.

Potassium Perchlorate, $KClO_4$.—The preparation of this salt by heating potassium chlorate has already been described and explained in vol. i., p. 324. It forms small rhombic crystals which possess a slightly saline taste. One part of the salt dissolves at 0° in 142·9, at 50° in 15·5, and at 100° in 5·04 parts of water (Muir); it is almost insoluble in strong alcohol, and is therefore used for the quantitative determination of potassium.

Potassium Bromate, $KBrO_3$, is obtained according to Stas, by passing chlorine into a warm solution of potassium bromide and caustic potash:

$$KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O.$$

A portion of the salt crystallises out on cooling, and the remainder is precipitated on addition of alcohol, together with a little potassium chloride, from which it is easily separated by recrystallisation. According to Marignac, it forms hexagonal crystals and separates out in six-sided tables or prisms which have the appearance of cubes. It is converted on ignition into potassium bromide and oxygen, bromine being also evolved when it is heated slowly.

Potassium Iodate, KIO_3, is formed together with the iodide by the action of iodine on caustic potash, but it is most readily obtained by heating potassium chlorate with iodine:

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2,$$

the liberated chlorine combines with excess of iodine to form iodine mono- and trichloride.[1] Potassium iodate crystallises in small cubical crystals, and only begins to decompose at a much higher temperature than the chlorate. It combines with iodic acid to form the compounds $KIO_3 + HIO_3$, and $KIO_3 + 2HIO_3$ (see vol. i., p. 333).

[1] Thorpe and Perry, *Journ. Chem. Soc.* 1892, i. 925.

Potassium Periodate, KIO_4, is formed when chlorine is passed through a mixture of caustic potash and potassium iodate. It separates out as shining crystals which are isomorphous with those of potassium perchlorate. When a hot concentrated solution of the salt is mixed with alcoholic potash, rhombohedra of *potassium meso-periodate*, $K_3IO_5 + 4H_2O$, are deposited. These have an alkaline reaction and absorb carbonic acid from the air. When the normal salt is evaporated together with caustic potash, asymmetric prisms of *potassium di-periodate*, $K_4I_2O_9 + 9H_2O$, are deposited, which have an alkaline reaction (see also vol. i., p. 335).

POTASSIUM AND SULPHUR

116 *Potassium Monosulphide*, K_2S.—This substance is formed, according to Berzelius, by leading hydrogen over potassium sulphate. It forms a pale red crystalline mass, which on heating becomes darker and melts to a black liquid below a red heat. Berthier obtained the same compound as a flesh-coloured mass by strongly heating the sulphate with carbon:

$$K_2SO_4 + 4C = K_2S + 4CO.$$

In order, however, to obtain this substance a larger amount of carbon is needed than that represented in the above equation, otherwise a mixture of higher sulphides with potassium carbonate is obtained (Wittstock). Indeed it appears impossible to obtain perfectly pure monosulphide, as even the substance obtained by reduction with hydrogen contains higher sulphur compounds.[1] The mass deliquesces in moist air, and dissolves in water with a considerable evolution of heat.

If potash lye be saturated with sulphuretted hydrogen, and if then an equal quantity of alkali be added to the solution, a solution of the monosulphide is obtained. This remains colourless if the air be excluded, possesses an alkaline taste, and acts on the skin as a strong caustic. When evaporated in a vacuum at a low temperature, four-sided prisms are deposited, having the formula $K_2S + 5H_2O$.[2] If this aqueous solution be boiled, sul-

[1] Bauer, *J. pr. Chem.* 1858, **75**, 246.
[2] Schöne, *Pogg. Ann.* 1867, **131**, 380.

phuretted hydrogen is given off, and when exposed to the air it becomes yellow from absorption of oxygen and carbon dioxide, and formation of potassium thiosulphate and potassium carbonate, the sulphuretted hydrogen which is liberated decomposing with formation of water and sulphur, and the latter substance uniting with the monosulphide to form higher sulphides. On shaking the yellow solution with metallic copper it again becomes colourless.

Potassium Hydrosulphide, KSH.—This substance was first prepared by Gay-Lussac by heating potassium in dry sulphuretted hydrogen. He then observed that the same quantity of potassium which was capable of evolving one volume of hydrogen from water was able to combine with all the sulphur in two volumes of sulphuretted hydrogen, liberating half the hydrogen:

$$2K + 2H_2S = H_2 + 2KSH.$$

Berzelius obtained the same compound by the action of sulphuretted hydrogen on carbonate of potassium heated to dull redness:

$$K_2CO_3 + 2H_2S = 2KSH + H_2O + CO_2.$$

This body forms a white or yellowish deliquescent mass, which when heated to dull redness melts to a liquid, and at a higher temperature becomes of a dark red colour. It is very soluble in water, and the aqueous solution is very easily obtained by saturating caustic potash solution with sulphuretted hydrogen. This forms a colourless liquid which smells slightly of sulphuretted hydrogen, has an alkaline and bitter taste, and on exposure to the air becomes yellow, owing to the formation of higher sulphides. When exposed a still longer time to the action of the air it becomes colourless, inasmuch as potassium thiosulphate is formed. If the concentrated solution be allowed to evaporate over caustic lime or caustic soda in a vacuum, colourless glittering rhombohedral crystals separate out, having the formula $2KSH + H_2O$.

In addition to these a number of polysulphides have been described, having the formulæ K_2S_2, K_2S_3, K_2S_4, and K_2S_5, which are obtained by the action of sulphur, sulphuretted hydrogen or carbon bisulphide vapour on the monosulphide, or compounds which readily yield it. They are described as yellowish-red or

dark red substances which dissolve readily in water. Spring and Demarteau,[1] however, regard these polysulphides as solid solutions of sulphur in the monosulphide, as in their reactions with iodine, potassium sulphite and ethyl iodide, they behave as mixtures of these two substances. They are also all reduced to the monosulphide when their solutions are shaken with mercury.

Liver of Sulphur or *Hepar Sulphuris.*—This is an old name given to a mixture of potassium polysulphides with potassium sulphate, or potassium thiosulphate. It is obtained by gently heating sulphur with carbonate of potassium in a covered vessel. The composition of the liver-coloured mass thus obtained is variable, according to the proportions in which the bodies have been mixed and the temperature to which they have been heated. Liver of sulphur was well known to the alchemists of the middle ages. Stahl considered it to be a compound of the alkali with sulphur, and called it "sulphurized alkali." He also knew that it could be prepared by heating sulphate of potash with carbon, and used this fact to prove that only one kind of phlogiston exists (see vol. i. p. 13). Liver of sulphur is used in medicine, and is termed in the Pharmacopœia, *potassa sulphurata.*

117 *Potassium sulphite,* K_2SO_3, is prepared by dissolving 100 grams of caustic potash in 200 cc. of water previously freed from dissolved air, and saturating with sulphur dioxide; a further quantity of 100 grams of caustic potash dissolved in a very small volume of water is then added, and the solution allowed to evaporate in vacuo. Potassium sulphite then separates in small deliquescent hexagonal crystals, which are more soluble in cold than in hot water. The *monohydrated salt* $K_2SO_3 + H_2O$ is obtained by dissolving the metabisulphite in water adding an equivalent quantity of caustic potash, evaporating and allowing to crystallise. The *dihydrated salt,* $K_2SO_3 + 2H_2O$, is obtained when the solution is allowed to evaporate over sulphuric acid, and forms oblique rhombic octohedra, which possess a bitter alkaline taste, and are also more soluble in cold than in hot water. The solutions readily undergo oxidation in the air.

Two isomeric potassium sodium sulphites $Na.SO_2.OK$ and $K.SO_2.ONa$ are also known. These have already been described in vol. i. p. 373.

Potassium hydrogen sulphite, $KHSO_3$, is produced when a solution of the normal salt or of caustic potash is saturated

[1] *Bull. Soc. Chim.* 1889 (3), **1**, 311.

with sulphur dioxide. On addition of alcohol it separates out in needle-shaped crystals, which taste of sulphurous acid, and have a neutral reaction.

Potassium metabisulphite, $K_2S_2O_5$, is formed when sulphur dioxide is passed into a hot saturated solution of potassium carbonate (Muspratt) or into a mixture of milk of lime and potassium sulphate (Boake and Roberts). It forms monosymmetric crystals which are with difficulty soluble in water and have an unpleasant acid taste.

118 *Potassium sulphate*, K_2SO_4.—The mode of preparing this salt was known as early as the fourteenth century. It was first obtained from the residues of the manufacture of *aqua fortis*, and afterwards by the action of sulphuric acid on crude potashes. Potassium sulphate is probably one of the salts whose constituents were first determined by analysis. Glauber, Boyle, and Tachenius were acquainted with its composition, and in the seventeenth century it was termed *arcanum* or *sal duplicatum*, because, according to the then prevalent ideas, it was made up of an acid salt and an alkaline salt. The decomposition of this salt into its constituent parts was at that time supposed to be a most difficult matter. Indeed, Stahl proposed the following question to the French Academy: How it is possible to decompose this salt instantly when held in the hand? Although none of the Academicians were able to answer this question, Stahl accomplished his purpose by adding nitrate of silver, which at once separated vitriolic acid from the alkali.

Potassium sulphate is found native in the lavas of Vesuvius, and as kainite, $K_2SO_4,MgSO_4,MgCl_2+5H_2O$, in the Stassfurt beds and in those of Kulusz. It is also obtained as a by-product in several chemical manufactures, as in that of potassium bichromate, and in the preparation of pure potash and the purification of crude potashes as well as in the lixiviation of kelp. In order to obtain this salt from kainite, the mineral is allowed to remain for some time exposed to the air; it deliquesces, and as soon as the soluble magnesium chloride has run off, the remaining salt is recrystallised from boiling water, so that on cooling the difficultly soluble sulphate separates out.

Potassium sulphate crystallises in small hard rhombic pyramids, Figs. 56 and 57, possessing a hexagonal or prismatic habit; it has a specific gravity of 2·648 and melts at 1078°. One hundred parts of water at 15° dissolve 10·3 parts of this salt,

whilst 26·7 parts dissolve in the same quantity of water at 102°. Aqueous alcohol dissolves it in quantities proportional to the amount of water which the alcohol contains. The salt is quite insoluble in a solution of caustic potash of specific gravity 1·35 (Liebig), and in absolute alcohol. It has a bitter saline taste and can be volatilised only at a very high temperature.

Potassium sulphate is used as a purgative and employed in large quantities for the manufacture of potash-alum and potassium carbonates. The mineral kainite is also largely used as a fertiliser.

Acid Potassium Sulphate, $\left.\begin{matrix}H\\K\end{matrix}\right\}SO_4$.—In 1754, Rouelle proved that in addition to the *arcanum duplicatum*, other salts exist containing an excess of acid chemically combined. Amongst

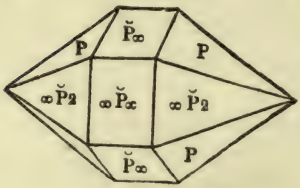


Fig. 56.

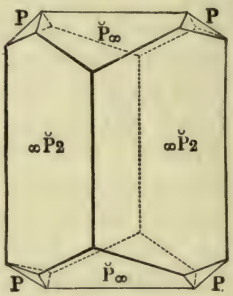


Fig. 57.

these he mentions acid potassium sulphate, which he obtained in the crystalline state. The same salt is found native in the Grotto del Sofo, near Naples, in the form of long silky needles. It is frequently prepared in the laboratory as a by-product in the manufacture of nitric acid from saltpetre and sulphuric acid. It crystallises in rhombic pyramids, according to Marignac, in rhombohedra according to Jacquelain, has a specific gravity of 2·163, melts at 197°, readily dissolves in water, and possesses an acid saline taste, and when brought into contact with alcohol it is decomposed into sulphuric acid and the normal salt which is insoluble in this liquid. When the acid sulphate is recrystallised from aqueous solution the normal salt is found to separate out first, then crystals of a salt having the composition $K_2SO_4+KHSO_4$ are deposited, and at last the acid sulphate crystallises out.

Potassium Disulphate, $K_2S_2O_7$.—This salt is obtained by gently igniting the normal salt with sulphuric acid until the mass fuses quietly. It is also formed when the acid salt is heated with potassium chlorosulphonate, a compound obtained by the action of sulphur trioxide on potassium chloride:

$$SO_2\begin{matrix}Cl\\OK\end{matrix} + SO_2\begin{matrix}OK\\OH\end{matrix} = \begin{matrix}SO_2—OK\\ \\SO_2—OK\end{matrix}\!\!>O + HCl.$$

The salt crystallises on cooling in long needles which decompose when brought into contact with water, evolving much heat and yielding the acid sulphate. When dissolved in fuming sulphuric acid this salt deposits transparent prismatic crystals of acid potassium disulphate, KHS_2O_7.

Potassium thiosulphate, $K_2S_2O_3$, is prepared in a similar manner to and closely resembles the corresponding sodium salt. Two isomeric sodium potassium thiosulphates are also known (vol. i., p. 414).

Potassium Persulphate, $K_2S_2O_8$.—This salt is obtained by the electrolysis of a saturated solution of potassium hydrogen sulphate, and forms large tabular crystals which are sparingly soluble in water. Details of its preparation and properties have already been given in vol. i., p. 411.

Potassium and Nitrogen.

119 *Potassamide*, NH_2K.—This compound was discovered by Gay-Lussac and Thénard in 1811. It is prepared by gently heating potassium in ammonia gas, and is usually obtained as an olive-green or brown mass, but when the potassium is heated in a silver boat, it forms a white waxy crystalline mass, which melts at 272—274° and sublimes above 400°.[1] It quickly decomposes in moist air, yielding caustic potash and ammonia, and when water is added the same decomposition takes place with rapid liberation of heat, and frequently also of light. When strongly heated it slowly undergoes decomposition into its elements, but does not, according to Titherley, leave a residue of the black potassium nitride described by Davy, which probably does not exist.

[1] Titherley, *Journ. Chem. Soc.* 1894, i. 511.

Potassium Nitrite, KNO_2, is formed when saltpetre is heated until one third of the oxygen is evolved (Mitscherlich). The residue invariably contains undecomposed nitrate, and also oxides of potassium. The above decomposition takes place more readily in the presence of metallic iron, copper or lead (Stromeyer). For this purpose two parts of lead may be employed to one part of saltpetre. The latter salt is fused, and the fused mass heated to dull redness, the lead then added little by little, and the cooled mass lixiviated with water. On evaporation, or on neutralising in the cold with dilute sulphuric acid and adding to the solution twice its weight of alcohol, crystals of the nitrite are precipitated.

Pure potassium nitrite is best prepared by decomposing silver nitrite with potassium chloride (Berzelius), or by decomposing amyl nitrite with the exactly necessary quantity of alcoholic potash (Chapman). It forms small indistinct crystals which deliquesce in moist air, and are insoluble in alcohol. This salt is employed for the separation of cobalt and nickel, and also in organic chemistry.

120 *Potassium Nitrate, Saltpetre or Nitre*, KNO_3.—This remarkable salt was known to the ancients, being termed *Sal petræ* by Geber. It was frequently called *Sal nitri* by the later alchemists, to distinguish it from *nitrum*, by which name the ancients signified the native carbonate of soda, a salt which was not unfrequently mistaken for nitre. When trade between the East and the West increased, the mineral alkali was imported under the special name of natron, and then the word nitrum was specially reserved to designate saltpetre.

Saltpetre occurs, together with other nitrates, as an efflorescence on the soil in various hot countries, especially in Bengal, but likewise in Egypt, Syria, Persia, and Hungary, as well as in America. In Ceylon,[1] and other parts of India, nitre is obtained by the lixiviation of certain porous rocks, whence the origin of the word sal-petræ. These yield from 2·5 to 8 per cent. of their weight of nitre. The formation of nitre, whether found in the soil or in porous felspathic rocks, is due to the gradual oxidation by the air of nitrogenous organic matter in contact with an alkali probably in presence of a nitrifying organism. In the decay and putrefaction of such bodies ammonia is first formed and nitric acid subsequently produced. Nitre is also found in the juices of certain plants. This fact was first pointed out by L. Lemery in 1717.

[1] John Davy, *Quart. Journ. Science*, 1818, **5**, 233.

Certain species of amaranthus, especially *A. atropurpureus*, contain no less than 22·7 per cent. of nitre in the dry plant (Boutin).

In India, a caste of men termed Sorawallahs,[1] from *sora*, nitre, make it the business of their lives to collect the raw material, and to manufacture and sell the salt, which is employed locally for producing frigorific mixtures and is also largely exported.

"The *Sorawallah* goes about the village, examining the small surface drains which issue from holes in the mud-wall, usually found around native dwellings and their cow-houses; when he detects a faint white veil-like patch of crystalline formation, on or near the dark-coloured borders of these little drains, he knows that a considerable quantity of nitre exists, on or near the surface of all the surrounding earth; he accordingly proceeds to scrape off a very thin layer of the surface soil, which he carries away to his place of manufacture, as soon as his morning's collections are finished. On arriving there, the impregnated earth so collected is thrown into an earthen vessel containing either water or water which has been poured off from previous supplies of similarly impregnated earth. When the water so used is pretty well saturated, it is poured into shallow pans of unglazed earthenware, in which it is then exposed to the combined influence of hot winds and the solar rays; these cause rapid evaporation, and the formation of crystals of nitrate of potash, which after one or two more crystallisations are ready for sale. The mother-liquor, on being further evaporated yields a proportion of common salt, varying from one to seven or nine per cent. The *Sorawallah* makes fresh collections from precisely the same spots of ground from week to week, year to year, and from generation to generation after the manner of the eastern world; the production of nitre is constant so long as the place continues to be inhabited; it even continues to appear in large, though gradually decreasing quantities, for years after the village may have been deserted. The intervals at which fresh collections may be made from the same spot vary in different localities and in different seasons of the year, from one to seven, ten, or more days."

This production of nitre is doubtless preceded by the formation of nitrate of calcium, and this, by double decomposition with potassium carbonate, yields nitre and calcium carbonate. Indian saltpetre was introduced into Europe by the Italians, and first employed for medicinal and chemical purposes.

[1] Palmer, *Journ. Chem. Soc.* 1869, 318.

When the demand for gunpowder became great, nitre began to be manufactured in Europe. Agricola, in his celebrated treatise *De Re Metallica*, describes the process of refining saltpetre as follows :—" Saltpetre is obtained from a dry somewhat fatty earth, which is boiled with quick-lime and wood-ashes. The mass is then lixiviated and the solution evaporated."[1] This process is employed to the present day, and during the blockade of the French ports, the artificial production of nitre was largely carried on in that country. In Sweden every landed proprietor is obliged to furnish the state with a certain quantity of nitre, and in Switzerland and other inland countries the manufacture of nitre is regularly carried on. For this purpose nitrogenous organic matter of animal or vegetable origin, after having been allowed to putrefy by exposure to air in a dark place, is mixed with substances such as lime, mortar, or wood-ashes, containing the carbonates of potash, magnesia, or lime. The mixture is then heaped together in ridges (saltpetre walls) or in low heaps (saltpetre mounds). These heaps are then moistened from time to time by the drainage of dung-heaps, or by urine, and exposed to the air. After standing for from two to three years the outer surface or saltpetre earth is removed and exhausted with water. This yields the crude saltpetre-ley which contains the nitrates of calcium and magnesium together with the chlorides of potassium and sodium. On boiling this liquor with potashes the calcium and magnesium salts are decomposed, and the clear solution is then crystallised. *Raw nitre* is thus obtained, and this by repeated solution and crystallisation is converted into *purified nitre*. The same process of purification is adopted in the case of the Indian saltpetre. Even when thus recrystallised the nitre is far from being chemically pure. In order still further to purify it, the salt is dissolved in boiling water, and the solution constantly agitated when cooling. The salt then separates out in small crystals termed *saltpetre-flour*, which inclose much less of the mother-liquor, and therefore much less impurity than the large crystals. This finely-divided salt may be still further purified by washing it with a saturated solution of pure nitre which dissolves out any foreign salts which may still be present, thus rendering the saltpetre free from chlorides and fit to be employed in gunpowder-making.

Since the discovery of large quantities of potassium chloride at Stassfurt, this salt has been largely used for the artificial

[1] Berzelius, *Traité*, **3**, 119.

manufacture of saltpetre. This manufacture depends upon the fact that under certain conditions of temperature and pressure, solutions of Chili saltpetre (sodium nitrate), $NaNO_3$, and of potassium chloride undergo, when mixed, a double decomposition, chloride of sodium being deposited and potassium nitrate remaining in solution. For this purpose equivalent quantities of sodium nitrate and potassium chloride are dissolved in the mother-liquor from a previous operation and heated by steam for about half an hour. The product is run into strainers where it is kept hot, the greater part of the sodium chloride separating out under these conditions; the filtered liquor is then allowed to cool, and the resulting saltpetre meal which contains 7 to 9 per cent. of sodium chloride and a little magnesium chloride purified by washing with mother-liquors re-

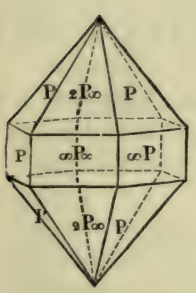


Fig. 58.

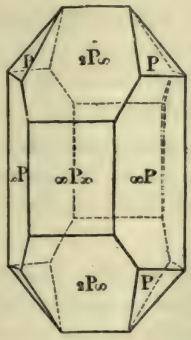


Fig. 59.

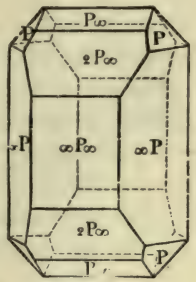


Fig. 60.

sulting from subsequent washings, recrystallised and finally washed with small quantities of pure water.

Saltpetre occurs in commerce in the form of small well-formed crystals, as well as in the form of flour. These are much purer than the larger crystals, which are often hollow and contain chloride of potassium and other impurities.

Potassium nitrate is dimorphous.[1] It usually crystallises in rhombic prisms (Figs. 58, 59, 60), which not unfrequently closely resemble regular six-sided prisms. If, however, a few drops of a solution of nitre be allowed slowly to evaporate, rhombohedral crystals are deposited, isomorphous with those of sodium nitrate, but these are very unstable and when touched are converted into an aggregate of small rhombic crystals.

[1] Miller, *Phil. Mag.* 1840 [3], **17**, 38.

Saltpetre has a specific gravity of 2·1; it melts at 339° (Person), 352° (Carnelley), and possesses a bitter cooling saline taste. It dissolves in water with absorption of much heat. This property of nitre was first pointed out by the Spanish physician Blasius Villafranca, in his tract published in 1550, entitled "Methodus refrigerandi ex vocato Sale-nitro vinum aquamque ac potus quodvis aliud genus." According to Rüdorff, 16 parts of nitre when dissolved in 100 parts of water at 13°·2 lower the temperature to + 3°.

The following table gives the solubility of saltpetre:

One hundred parts by weight of water dissolve at—

0°	10°	20°	30°	40°	50°
13·3	21·1	31·2	44·5	64	86 parts of nitre.
60°	70°	80°	90°	100°	
111	139	172	206	247 parts of nitre,	

whilst at 114°, the boiling-point of the saturated solution, 327·4 parts of the salt are dissolved.

Saltpetre is used in the laboratory, in medicine, for the salting or pickling of meat, to which it imparts a red colour, for pyrotechnic purposes, but chiefly in the manufacture of gunpowder.

Nitre used as an Explosive.—The Chinese are said to have been acquainted with the mode of manufacturing gunpowder from early times, although employing it rather for making fireworks than for warlike purposes. It appears probable that the knowledge of this manufacture resulted from an improvement in the preparation of Greek fire, which was discovered in 673 A.D., and itself consisted of combustible and fusible substances such as pitch, resin and sulphur mingled with crude saltpetre. In the *Liber ignium* of Marcus Graecus, a work which dates from the early part of the thirteenth century, and bears many traces of Arabian influence, mention is made of the use of saltpetre, *sal petrosum*, as a constituent of gunpowder. None of the Arabian alchemists appear to have been aware of the property of saltpetre to deflagrate when mixed with a combustible body, and not until the thirteenth century do we find this clearly pointed out by Roger Bacon as follows:—[1] "Talis natura est (sal nitrum), quod si immediate ignitos carbones tangat, statim accensum impetu evolat."

[1] Breve breviarum de Dono Dei.

This fact is strikingly shown when a mixture of twenty parts of nitre and three parts of charcoal is thrown into a red-hot crucible; vivid incandescence and a violent combustion being noticed:

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2.$$

An intimate mixture of fifteen parts of saltpetre and five parts of sulphur also burns very brilliantly:

$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2.$$

Detonating Powder, first described by Glauber, consists of a mixture of three parts of saltpetre, two parts of dry carbonate of potash, and one part of sulphur. When this mixture is heated in an iron spoon it first fuses and then explodes violently. In this reaction the sulphur forms potassium sulphide, which at the high temperature of the combustion is oxidised by the nitre, free nitrogen being evolved.

Powder of Fusion, or *Baumé's Quick Flux*, also mentioned by Glauber, contains one part of nitre, one part of sulphur, and one of sawdust. This if set on fire burns with so much heat that a small silver coin exposed to it is melted in a moment.

121 *Gunpowder.*—Fire-arms appear to have been used in Florence in 1325, but field-pieces were first employed by the English at the battle of Crécy in 1346.

Gunpowder consists of a mixture, in somewhat varying proportions, of charcoal, sulphur and nitre. Its explosive power depends on the rapid combustion of the charcoal and sulphur at the expense of the oxygen of the nitre, and the sudden liberation of a large volume of gas, which occupies several hundred times the bulk of the solid powder. Hence gunpowder can burn in a closed space or under water, as it contains the oxygen needed for the combustion in itself. It is a singular fact that it has been found in practice that the description of gunpowder which acts best is that which contains nearly two molecules of nitre to one atom of sulphur and three of carbon. Hence it was formerly believed that the decomposition which takes place when powder is fired is a very simple one, represented by the following equation:

$$2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2.$$

If this equation represents the decomposition which actually occurs, it follows that the most effective powder must be composed of:

Nitre	74·9
Carbon	13·3
Sulphur	11·8
	100·0.

The compositions of the gunpowders employed by different nations approach closely to these theoretical numbers; but in no case, as will hereafter be seen, are these numbers exactly adhered to. Indeed the fact that the charcoal employed in the manufacture of gunpowder does not consist of pure carbon, but contains considerable quantities of hydrogen and oxygen, is sufficient to show that the above simple reaction cannot represent the real decomposition which occurs when powder is fired. In addition to this, however, Gay-Lussac and Chevreul proved long ago that, in addition to nitrogen and carbon dioxide, carbon monoxide is evolved in the firing of gunpowder, whilst the residue does not merely consist of potassium sulphide, but contains the carbonate, sulphate, and other salts.

We owe the first careful experimental investigation concerning the nature of the decompositions which occur when powder is fired to Bunsen and Schischkoff.[1] They proved that a very large number of salts, such as sulphate, thiosulphate, sulphide, and carbonate of potassium, are contained in the smoke and solid residue remaining after the powder has been fired; whilst many other gases, especially carbon monoxide, hydrogen and sulphuretted hydrogen, besides carbon dioxide and nitrogen, are formed. In these experiments the powder was fired into a vacuum, and consequently some conditions as regards temperature and pressure which are met with in the practical use of gunpowder were not maintained. Linck repeated these experiments with a different kind of powder, and Karolyi analysed the products obtained by exploding small charges in shells inclosed in a vacuous space.

Subsequently Abel and Noble[2] published the results of a very complete investigation on the products of combustion of powder fired under conditions similar to those which exist when

[1] *Phil Mag.* 1858, (4), **15**, 489.
[2] *Phil. Trans.* 1874. Part II., 49.

it is fired in guns. The gunpowder operated upon included five kinds, viz. pebble powder, rifle large-grain (cannon powder), fine-grain powder, and rifle fine-grain powder, all English military powders, together with one spherical pellet powder of Spanish manufacture. The following table gives the complete analyses of the different powders employed:—

	Pebble powder. Waltham Abbey.	Rifle large-grain (cannon powder). Waltham Abbey.	Rifle fine-grain. Waltham Abbey.	Fine-grain. Waltham Abbey.	Spanish spherical pebble-powder.
Saltpetre	74·67	74·95	75·04	73·55	75·30
Potassium sulphate	0·09	0·15	0·14	0·36	0·27
Potassium chloride	—	—	—	—	0·02
Sulphur	10·07	10·27	9·93	10·02	12·42
Charcoal: Carbon	12·12	10·86	10·67	11·36	8·65
Charcoal: Hydrogen	0·42	0·42	0·52	0·49	0·38
Charcoal: Oxygen	1·45	1·99	2·66	2·57	1·68
Charcoal: Ash	0·23	0·25	0·24	0·17	0·63
Charcoal: total	14·22	13·52	14·09	14·59	11·34
Water	0·95	1·11	0·80	1·48	0·65

The quantities of gunpowder exploded in the several operations varied from 100 to 750 grams. The apparatus in which the charges were exploded consisted of a mild steel vessel of great strength, carefully tempered in oil. The charge to be exploded was placed in the chamber of this steel vessel, and the main orifice of the vessel was closed by a screw plug, called the firing-plug, which fitted into its place with great accuracy. In this firing-plug itself was a conical hole, also stopped by a plug, and through this passed two insulated platinum wires, by means of which the charge could be fired by electricity. Two other apertures were made in the chamber; one of these communicated with the arrangement for allowing the gases to escape; the other contained an apparatus for determining the tension of the gases at the moment of explosion. The pressures actually observed varied from one to 36 tons on the square inch, the whole of the gaseous products remaining pent-up in the cylinder under this enormous pressure. The results of this investigation may be shortly stated as follows:—

(1). The composition of the *gas* furnished by the explosion of all the English powders is remarkably uniform, but under high

pressures the carbon dioxide increases and the carbon monoxide decreases.

(2). The composition of the *solid* products exhibits a much greater variation.

(3). The decomposition which an average gunpowder undergoes when fired in a closed space cannot be represented by even a comparatively complicated chemical equation.

(4). The volume of the permanent gases measured at 0° and 760 mm. furnished by the combustion of one gram of powder in a closed vessel is about 280 cc., and is therefore about 280 times the volume of the powder.

(5). When 1 gram of powder is burnt the solid products of combustion amount to 0·57 gram, and the permanently gaseous products 0·43 gram.

(6). The tension of the products of combustion when the powder entirely fills the space in which it is fired is about 6,400 atmospheres, or 42 tons per square inch.

(7). The heat developed by the burning of 1 gram of powder is about 705 thermal units.

(8). The temperature of explosion is about 2,200° C.

The following tables give the analytical results obtained, including the percentage composition of the products of combustion of three of the powders:—

I. (Pebble); II. R. L. G. (Rifle Large Grain); III. F. G. (Fine Grain), each under two different pressures.

	Pebble. I.		R. L. G. II.		F. G. III.	
Pressure of explosion in tons per square inch. .	1·4	12·5	1·6	35·6	3·7	18·2
Percentage weight of solid products	56·12	55·17	57·22	57·14	58·17	58·09
Percentage weight of gaseous products	43·88	44·83	42·78	42·86	41·83	41·92

Percentage Weights of Solid Products of Combustion.

Potassium carbonate	55·50	56·15	52·56	65·71	59·39	43·03
sulphate . .	15·02	11·93	20·47	8·52	24·22	21·00
thiosulphate .	20·73	6·12	20·37	8·59	5·30	32·07
monosulphide .	7·41	19·12	4·02	7·23	5·12	—
thiocyanate .	0·09	0·23	trace	0·36	0·02	0·23
nitrate . . .	0·48	0·20	0·56	0·19	0·08	0·19
oxide . . .	—	—	—	—	—	2·98
Ammonium sesqui-carbonate . .	0·16	0·08	0·06	0·18	0·15	0·03
Sulphur	0·61	6·17	1·25	9·22	5·72	0·47
Carbon	trace	trace	0·71	—	trace	trace

Percentage Volumes of Gaseous Products.

Carbon dioxide . .	46·66	49·82	48·99	51·79	47·41	53·02
Carbon monoxide .	14·76	13·36	8·98	8·32	12·35	7·91
Nitrogen	32·75	32·19	35·60	34·64	32·35	34·20
Sulphuretted hydrogen . . .	3·13	1·96	4·06	2·61	3·76	2·03
Marsh gas. . . .	—	0·58	0·29	0·41	—	0·50
Hydrogen. . . .	2·70	2·08	2·07	2·04	4·13	2·13
Oxygen	—	—	—	0·18	—	0·15

COMPOSITION BY WEIGHT (IN GRAMS) OF THE PRODUCTS OF EXPLOSION OF A GRAM OF POWDER AS FURNISHED BY THE ABOVE EXAMPLES.

	I.		II.		III.	
Potassium carbonate	0·3115	0·3098	0·3007	0·3755	0·3454	0·2499
thiosulphate .	0·1163	0·0338	0·1166	0·0491	0·0308	0·1863
sulphate . .	0·0843	0·0658	0·1171	0·0487	0·1409	0·1220
sulphide . .	0·0416	0·1055	0·0230	0·0413	0·0298	—
thiocyanate .	0·0005	0·0013	0·0000	0·0021	0·0001	0·0013
nitrate . . .	0·0027	0·0011	0·0032	0·0011	0·0005	0·0011
oxide . . .	—	—	—	—	—	0·0173
Ammonium sesqui-carbonate . .	0·0009	0·0004	0·0003	0·0009	0·0009	0·0002
Carbon	—	—	0·0072	—	—	—
Sulphur	0·0034	0·0340	0·0041	0·0527	0·0333	0·0027
Total solid . .	0·5612	0·5517	0·5722	0·5714	0·5817	0·5808

Sulphuretted hydrogen	0·0134	0·0084	0·0166	0·0077	0·0154	0·0081
Oxygen	—	—	—	—	—	0·0006
Carbon monoxide	0·0519	0·0473	0·0303	0·0356	0·0416	0·0258
Carbon dioxide	0·2577	0·2770	0·2597	0·2750	0·2512	0·2718
Marsh gas	—	0·0012	0·0006	0·0015	—	0·0009
Hydrogen	0·0007	0·0005	0·0005	0·0003	0·0010	0·0005
Nitrogen	0·1151	0·1139	0·1201	0·1085	0·1091	0·1117
Total gaseous	0·4388	0·4483	0·4278	0·4286	0·4183	0·4192

The total theoretic work of gunpowder is about 332,000 gram metres per gram, or 486 foot-tons per lb. of powder.

A difference between the products of powder of large- and small-grain can be observed. The very small-grain powders furnish decidedly smaller proportions of gaseous products than a large-grain powder, and this again smaller than a pebble powder. The most important solid products are found to consist of the following potassium salts: carbonate, sulphate, thiosulphate and sulphide. The proportion of carbonate is much larger, and that of sulphate very much smaller, than had been formerly believed to be the case.

Potassium and Phosphorus.

122 *Normal Potassium Ortho-Phosphate*, K_3PO_4, is formed, according to Graham, when phosphoric acid is ignited with an excess of potassium carbonate. It is readily soluble in water, and crystallizes in small needles. The mono-acid salt K_2HPO_4 does not crystallise (Graham), and the diacid salt KH_2PO_4 is obtained by adding phosphoric acid to a solution of carbonate of potash until the liquid turns blue litmus red, and this on drying is again turned blue. The salt is deposited in quadratic crystals easily soluble in water but insoluble in alchohol.

Potassium Pyrophosphate, $K_4P_2O_7$.—When the mono-acid orthophosphate is ignited this salt is formed. It deliquesces on exposure, and is deposited in the form of fibrous crystals containing three molecules of water, when the solution is evaporated. The acid salt, $H_2K_2P_2O_7$, separates out as a white deliquescent mass when the normal pyro-salt is dissolved in acetic acid and alcohol added to the solution.

Potassium metaphosphates.—These salts exist in a large number of polymeric modifications, which closely resemble the corresponding sodium salts (p. 182).

Potassium and Arsenic.

123 *Potassium Arsenite.*—Arsenic trioxide dissolves easily in an aqueous solution of potash, and if the minimum quantity of potash be employed, the compound $KAsO_2 + H_3AsO_3$ may be obtained as a crystalline powder when the solution is mixed with alcohol. If this is warmed with a solution of potassium carbonate, potassium meta-arsenite, $KAsO_2$, is formed, and this when warmed with caustic potash yields potassium diarsenite, $K_4As_2O_5$, likewise precipitable by alcohol.

A solution of potassium arsenite is used in medicine under the name of Fowler's Solution. This solution is prepared by boiling one part of solid arsenic trioxide with an equal weight of potassium carbonate in distilled water, and diluting the clear liquid so as to form 90 parts of solution.

Normal Potassium Arsenate, K_3AsO_4, is prepared by adding an excess of caustic potash to arsenic acid. On evaporation it is deposited in the crystalline form (Graham). Mono-acid potassium arsenate, K_2HAsO_4, crystallises with difficulty, but the diacid salt, KH_2AsO_4, can be obtained in large crystals. This last salt was known as *Macquer's arsenikalisches Mittelsalz*, and was formerly prepared by deflagrating equal parts of arsenious acid and nitre, dissolving in water, and leaving the solution to crystallise. These crystals are isomorphous with diacid potassium phosphate, and like these turn blue litmus-paper red, but this red colour disappears on drying.

Potassium and Carbon.

124 *Normal Potassium Carbonate*, K_2CO_3.—This salt, well-known under the name of potashes, was originally obtained solely from the ashes of wood and other land plants, as the name implies, boiled in pots. Even to the present day this compound is largely obtained according to the old process, especially in Canada, North America, Moravia, the Steppes of Southern Russia, Hungary, and other districts where wood is

plentiful. The ashes are lixiviated in wooden tubs, and the dark brown lye thus obtained evaporated to dryness or to the point of crystallisation, and the residue calcined in a reverberatory furnace to remove organic matter. The crude product has usually a red, yellow, or green colour, due to the presence of iron or manganese, and also contains potassium chloride, sulphate and silicate, as well as sodium salts, and, where caustic lime is added, as in the preparation of American potash, considerable quantities of caustic potash; the latter may be converted into carbonate by calcining the crude ash with sawdust. To purify the crude ash it is redissolved in two parts of boiling water, the filtered solution allowed to stand for some days, then poured off from separated salts, chiefly consisting of potassium sulphate, and the clear solution evaporated till salt commences to crystallise out. After cooling, the salt is drained and washed with small quantities of water to remove the adherent mother-liquor. To the white salt thus obtained the name *pearl-ash* is given.

During the last half century, owing to the high price of potashes and the gradual extinction of forests, and in consequence of this alkali being a substance largely needed in manufacturing processes, other sources of potassium compounds have been sought. The suggestion has frequently been made that felspar and other silicates of potash should be employed for the purpose, and this proposition seems a very plausible one, inasmuch as it is by the slow decomposition of these silicates that all fruitful soils obtain their potash salts. At the same time, experience has shown it to be impossible to obtain potash from this source, and fortunately other richer sources of potassium compounds have been discovered. Amongst these the first to be noted is that from the manufacture of beet-root and cane-sugar. Beet-root is a potash plant, its ash being particularly rich in potassium compounds. The first attempt to obtain potash from this plant was that of incinerating the leaves. This process however did not prove available, and it was afterwards suggested that the molasses or uncrystallisable sugar, which also contains large quantities of potash salts, should be first allowed to ferment, whereby the sugar is converted into alcohol, and the liquors evaporated. In this way a black mass is obtained, consisting of alkaline salts together with carbon. On lixiviation a solution is obtained, and this is evaporated until it attains a specific gravity of

1·25—1·30. Potassium sulphate separates out together with sodium carbonate. The hot lye is then drawn off, and, on cooling, potassium chloride is obtained, together with some potassium sulphate. Further evaporation and cooling yields a mass which chiefly contains the carbonates of potash and of soda, together with a little potassium chloride and sulphate. These raw beet-root potashes are termed "salin" on the Continent. This crude material is again lixiviated and the liquors are boiled down again, and a repetition of this process is carried on until the material contains 82—84 per cent. of potassium carbonate. The potashes obtained by this process vary very much in quality, according to the district where the beet-root has been grown. They are richer where the beet-root has been recently introduced than where the soil has been partially exhausted.

Another remarkable source of potassium is that from sheep-wool. It has already been mentioned that sheep withdraw a considerable quantity of potash salts from the soil. Chevreul first pointed out that the sweat or suint of sheep contains no less than one-third of its weight of potash salts. The brown liquors in which the wool has been washed are evaporated to dryness, and the solid residue calcined in retorts, by which means ammonia and a gas used for illuminating purposes are evolved; the residual mixture of charcoal and alkaline salts is again lixiviated and treated in a similar way to the salin already described.

Potashes are lastly manufactured on a still larger scale from potassium sulphate, which is obtained in considerable quantity both from the Stassfurt beds and from sea-water. A large quantity is also obtained by heating potassium chloride with sulphuric acid, and in the manufacture of bichrome. For the purpose of converting the sulphate into the carbonate it is heated in a reverberatory (black-ash) furnace with the requisite quantity of limestone and coal, the product being worked exactly according to Leblanc's process for obtaining carbonate of soda from salt-cake (p. 197).

In order to prepare chemically pure potassium carbonate, it was customary formerly to employ pure cream of tartar (hydrogen potassium tartrate) which was heated in covered iron crucibles. A mixture of carbon and potassium carbonate was thus obtained, and by lixiviating the residue with water and evaporating the solution down in a silver basin the pure

salt was deposited. This salt even now retains the name of salt of tartar. Instead of the expensive tartar it is now customary to employ the much cheaper hydrogen potassium carbonate or bicarbonate of potash, which can be easily prepared in the pure state, and which on heating yields water, carbon dioxide, and potassium carbonate:

$$2KHCO_3 = H_2O + CO_2 + K_2CO_3$$

When prepared on the manufacturing scale, the carbonic acid which is evolved is made use of for the preparation of a fresh portion of bicarbonate.

Pure potassium carbonate occurs either in the form of a white granular powder or as a white solid mass which possesses a strong alkaline reaction and has an alkaline and slightly caustic taste. It melts at 879°, and then loses a small quantity of carbon dioxide, and is converted into caustic potash and carbon dioxide at a red heat in a current of steam or hydrogen. At a white heat it is volatilised. It is extremely hygroscopic and very soluble in water, and when exposed to the air it soon deliquesces to an oily liquid which has received the name of "oleum tartari per deliquium." According to Mulder, 100 parts of water dissolve the following quantity of salt at—

0°	20°	40°	60°	80°
89·4	112	117	127	140 parts.

At 135°, the boiling point of the saturated solution, 100 parts of water dissolve 205 parts of the salt. For the specific gravity of solutions of this salt, Gerlach's tables may be consulted.[1] When the concentrated solution is allowed to stand monosymmetric crystals possessing a glassy appearance and having the composition $2K_2CO_3 + 3H_2O$ are deposited. These on heating to 100° fall to a white powder having the composition, $K_2CO_3 + H_2O$, and this at 130° loses all its water.

Potassium carbonate is largely used in the manufacture of soft-soap, potassium ferrocyanide and chromate, and crystal glass.

Hydrogen Potassium Carbonate, $KHCO_3$.—This salt, also known as bicarbonate of potassium, is obtained by passing carbon dioxide through a concentrated solution of the normal salt when the bicarbonate, which is much less soluble, crystallises out. Another

[1] *Zeit. Analyt. Chem.* 1869, 8, 279.

process is to pass a current of carbon dioxide over the slightly moistened purified potashes, the product being recrystallised from warm water. It forms large transparent crystals belonging to the monosymmetric system, which possess a saline taste and a slightly alkaline reaction. 100 parts of water dissolve at the ordinary temperature, about 25 parts, and at 70° 45 parts, of the salt. When the solution is boiled carbon dioxide is given off, and when the dry salt is heated to 190° it is completely decomposed into the normal carbonate and carbon dioxide.

125 *Potassium Cyanide*, KCN.—Commercial potassium cyanide is prepared according to Liebig's method as follows. Eight parts of dry ferrocyanide of potassium are melted in an iron crucible together with three parts of potassium carbonate:

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KOCN + CO_2 + Fe.$$

As is seen in the above equation, the cyanide thus prepared contains a small quantity of cyanate. For many purposes this admixture is of no consequence. A purer product can be obtained by heating the dry ferrocyanide to a bright red heat:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

To avoid the loss of cyanogen which thus takes place in both these reactions it is now usual to treat the ferrocyanide with metallic sodium:

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

The resulting mixture of potassium and sodium cyanides is known commercially as potassium cyanide. Chemically pure potassium cyanide is best prepared by passing the vapour of hydrocyanic acid into an alcoholic solution of potash, the salt then separating out as a white crystalline powder.

Potassium cyanide has a sharp bitter taste; it is exceedingly soluble in water and dissolves slightly in cold, and somewhat more readily in hot, alcohol. When the concentrated aqueous solution of the salt is allowed to evaporate over strong sulphuric acid it deposits crystals in the form of regular octohedra. Potassium cyanide is readily fusible, and on cooling solidifies in cubes. The weakest acids, even carbonic acid, decompose the salt with evolution of hydrocyanic acid. The salt is, more-

over, partially hydrolysed in its aqueous solution (p. 89), which possesses an alkaline reaction and always smells of hydrocyanic acid. It is itself as poisonous as the acid.

Potassium cyanide is used in very large quantity in the McArthur-Forrest process for recovering the last portions of gold from the tailings of the gold mines,[1] and in the laboratory, where it is used as a reducing agent. This is due to the fact that when in the fused state it withdraws oxygen from many oxides and is converted into potassium cyanate. When heated with nitric acid or potassium chlorate violent explosions occur. Potassium cyanide and sulphur when melted together combine directly, forming potassium thiocyanate. This compound is also formed when the cyanide is heated with several metallic sulphides.

Potassium Cyanate, KCNO or CO:NK, is prepared by heating four parts of very carefully dried potassium ferrocyanide and three parts of fused potassium bichromate in an iron dish and extracting the product with 80 per cent. methylated spirit. It crystallises on evaporating the alcoholic solution in transparent plates, which are readily soluble in water and alcohol, the aqueous solution gradually decomposing into ammonia and potassium hydrogen carbonate:

$$KCNO + 2H_2O = NH_3 + KHCO_3.$$

Potassium cyanate is employed in the preparation of certain organic compounds.

Potassium Thiocyanate, KCNS or CS:NK is formed by the direct union of potassium cyanide and sulphur, but is usually prepared by gently heating a mixture of 46 parts of dry potassium ferrocyanide, 17 parts of potassium carbonate, and 32 parts of sulphur. The mass after cooling is extracted with boiling alcohol, and crystallises from the cooled solution in long striated prisms, which readily melt when heated and deliquesce in moist air. It is very soluble in water, with considerable absorption of heat; thus if 500 grams of the salt be mixed with 400 grams of water the temperature of the mass sinks to −20°, and hence the salt is used as a refrigerant.

[1] *Journ. Soc. Chem. Ind.* 1890, 270; Maclaurin, *Journ. Chem. Soc.* 1893, i. 724; 1895, i. 199.

Potassium and Silicon.

126 *Potassium Silicates.*—When silica is fused with potassium carbonate, carbon dioxide is evolved, and according to the proportions of the two substances employed, the temperature, and the length of heating, the silicates K_2SiO_3, $K_4Si_3O_8(2K_2O, 3SiO_2)$, and $K_8Si_3O_{10}(4K_2O, 3SiO_2)$ are obtained.[1] Attempts to obtain the orthosilicate K_4SiO_4 have all been unsuccessful, and in all probability it does not exist.

Potassium Metasilicate, K_2SiO_3, obtained by fusing equal molecular proportions of silica and potassium carbonate, forms a glassy mass which deliquesces on exposure to moist air. It also absorbs carbonic acid from the air, and is gradually transformed into a transparent jelly which in time shrinks together, and after some weeks becomes hard enough to scratch glass. It is probable that opal and flint are formed in a similar manner (Kuhlmann). Van Helmont was aware that the substance obtained by fusing silica with an excess of alkali became liquid on exposure to air, and Glauber termed this *liquor silicum.*

Soluble Glass.—This substance was discovered by Fuchs in 1818, and is manufactured by fusing 45 parts of quartz, 30 of potashes, and 3 of powdered charcoal, for from 5 to 6 hours. The charcoal serves to assist the evolution of carbon dioxide which is thereby reduced to carbonic oxide. The hard, greyish, and vitreous mass is dissolved in water, and the clear solution evaporated down. It forms a clear, glassy mass, which only fuses with difficulty, and dissolves slowly but completely in 5 parts of water.

Numerous precipitates of constant composition have been obtained from the solution, but it is uncertain whether these are definite compounds. Among them may be mentioned $K_4Si_9O_{20}$ $(2K_2O,9SiO_2)$, $K_2Si_4O_9$ $(K_2O,4SiO_2)$, and $K_2Si_8O_{17}$ $(K_2O,8SiO_2)$.

Soluble potash glass is used for a variety of purposes, but its place has mostly been taken by the cheaper soda glass, also discovered by Fuchs (p. 217).

Potassium Fluosilicate, K_2SiF_6, is obtained when hydrofluosilicic acid is brought into contact with a solution of a potassium salt. When the acid is added in small quantities

[1] Scheerer, *Annalen*, 1860, **116**, 149.

no precipitate is observed to form, but soon the liquid begins to exhibit iridescent colours, and after a while the insoluble potassium fluosilicate separates out as a semi-transparent mass. After washing with water and drying, the salt is obtained as a fine white powder difficultly soluble in cold, though easily soluble in hot water. By slow cooling it may be obtained in the form of bright octohedra, which sometimes show cubic faces (Marignac).

Potassium and Boron.

127 *Potassium Metaborate*, KBO_2.—When boric acid and potassium carbonate (or any other potash salt containing a volatile acid) are fused together in the proper proportions the above salt is obtained. It is difficultly soluble in water, and is deposited in small monosymmetric crystals, possesses an alkaline reaction, and absorbs carbonic acid from the air with formation of potassium pyroborate or tetraborate. This latter substance is obtained by adding caustic potash to a solution of boric acid until the liquid attains an alkaline reaction. It is easily soluble, crystallises in hexagonal prisms having the formula $K_2B_4O_7 + 5H_2O$, and possesses a faint alkaline taste. If hot solutions of boric acid and potassium carbonate be mixed together, in the proportion of one molecule of the former to two molecules of the latter, glittering rhombic crystals of *potassium triborate*, $2KB_3O_5 + 5H_2O$, separate out, and when a hot solution of caustic potash is saturated with boric acid, rhombic pyramids of *potassium pentaborate*, $KB_5O_8 + 4H_2O$, are deposited.

Detection and Estimation of Potassium and its Compounds.

128 The best indication of the presence of potassium compounds is the violet colour which they impart to the non-luminous flame. This tint is, however, not seen if even a small quantity of a sodium compound be present, and it is then necessary to examine the flame by means of the spectroscope. The spectrum thus obtained is that of the metal itself, and contains only two characteristic lines:—viz., the double line K *a* (7699 and 7665), in the outermost red, approaching the

ultra red rays and somewhat below the dark line A of the solar spectrum; and a second line K β (4044), situated far in the violet rays, towards the other end of the spectrum, also identical with a dark solar line. Owing to the position of the two lines, K α and K β, both situated near the limit at which our eyes cease to be sensitive to the rays, this reaction for potassium is not very sensitive, but $\frac{1}{1000}$ of a milligram can be readily detected. The absorption spectrum of potassium has been mapped by Roscoe and Schuster.[1] It is totally different from the emission spectrum just described, being a channelled space spectrum. Observed at a low temperature the green-coloured vapour exhibits a well-marked series of bands, one group in the red (α) and two groups (β and γ) at each side of the sodium line being seen. These bands are all shaded off towards the red, and in general appearance resemble those of the iodine spectrum.

In order to separate soluble potassium compounds from other metallic salts, they must be precipitated either as the perchlorate, the acid tartrate, or the platinochloride K_2PtCl_6.

For the separation of this metal from sodium and for its quantitative estimation, an excess of platinum tetrachloride is added to the mixed chlorides, the liquid then evaporated on the water-bath, and the cooled residue mixed with strong alcohol, in which the excess of platinic chloride and the sodium double-salt easily dissolve. The potassium double-salt is then collected, dried and weighed. The potassium may also be estimated by adding perchloric acid and alcohol to the concentrated solution, the precipitated potassium perchlorate being washed with a mixture of alcohol and water, dried and weighed.

The mixed chlorides of potassium and sodium can also be weighed, and then converted into sulphates by treatment with strong sulphuric acid, and the weight of these determined. From these data the amount of potassium (x) and of sodium (y) present can readily be calculated when the molecular weights of the several salts are known. Thus:

$K = 38{\cdot}85$	$Na = 22{\cdot}87$	$K_2 = 77{\cdot}70$	$Na_2 = 45{\cdot}74$
$Cl = 35{\cdot}19$	$Cl = 35{\cdot}19$	$SO_4 = 95{\cdot}34$	$SO_4 = 95{\cdot}34$
74·04	58·06	173·04	141·08

[1] *Proc. Roy. Soc.* 1874, 362.

If A represent the weight of the mixed chlorides, and B that of the mixed sulphates, we have:

$$A = \frac{74{\cdot}04}{38{\cdot}85}x + \frac{58{\cdot}06}{22{\cdot}87}y.$$

$$B = \frac{173{\cdot}04}{77{\cdot}70}x + \frac{141{\cdot}08}{45{\cdot}74}y.$$

From which the values of x and y can be readily obtained.

A similar result may be obtained by simply ascertaining the amount of chlorine present in the mixed chlorides by titration with silver nitrate solution, but neither of these indirect methods is susceptible of great accuracy.

The atomic weight of potassium has been most accurately determined by Stas. As a mean of eight experiments he found that 100 parts of potassium chlorate yielded 60·846 parts of potassium chloride on ignition. Moreover, 69·103 parts of potassium chloride were needed, as a mean of nineteen experiments, to precipitate 100 parts of silver from solution; and 100 parts of silver, as a mean of seven experiments, gave 132·8445 parts of silver chloride. These experiments give the number 38·85 as the mean for the atomic weight of potassium, the number 35·19 for that of chlorine, and the number 107·13 for that of silver when O = 15·88.

LITHIUM, Li = 6·98.

129 Lithium was discovered in 1817 by Aug. Arfvedson, whilst he was working in the laboratory of Berzelius.[1] He obtained a new alkali, and Berzelius gave to it the name *lithia*. It was first found in several minerals, from the iron mines of Utö in Sweden, especially petalite and spodumene.

Lithium is derived from λίθεος, stony, as it was then believed to be an alkali whose presence was confined to mineral matter in contradistinction to the other alkalis which were found in vegetable and animal bodies. Since that time, however, lithium has been shown to be very generally distributed throughout the animal and vegetable kingdoms. The general distribution of small quantities of lithium compounds was first ascertained by

[1] *Schw.* **22**, 93; *Ann. Chim. Phys.* **10**, 82.

Bunsen and Kirchhoff in their first research on spectrum analysis in 1860 (p. 139).[1]

Sources of Lithium.—The most important minerals containing this element are *triphyline*, a phosphate of iron, manganese, and lithium, $(LiNa)_3PO_4+(FeMn)_3(PO_4)_2$, containing from 1·6 to 3·7 per cent. of lithium; *petalite*, a silicate of aluminium, sodium, and lithium, containing 2·7 to 3·7 per cent. of lithium; *lepidolite* or *lithia-mica* 1·3 to 5·7 per cent.; *spodumene* or *triphane*, a silicate of aluminium, sodium, and lithium, 3·8 to 5·6 per cent. Smaller quantities of lithium, whose presence can be ascertained by the spectroscope, are found in a large number of minerals. The water of certain mineral springs also contains large quantities of dissolved lithium salts. Thus Berzelius[2] so long ago as 1822 detected this element in the water of Egger-Franzensbad, and in 1825 in the springs at Karlsbad and Marienbad. The spectroscope has since shown that lithium occurs in most mineral waters, in sea-water, and in that of almost every river[3] and surface spring. Some mineral springs contain lithium in considerable quantity. Thus Bunsen found 295·2 mgrm. of lithium chloride in one liter of the water of the Mur-spring at Baden-Baden,[4] and W. A. Miller[5] found 372 mgrm. in one liter of water from a spring in the Wheal Clifford mine at Redruth in Cornwall.

By the decomposition of rocks containing lithium this metal finds its way into the soil. It has been detected in that of the Limagne d'Auvergne, and can be traced in the ashes of the plants which grow in that district (Truchot).[6] It is widely distributed throughout the vegetable kingdom, occurring in the ash of the vine, in that of many cereals, in sea-weed and in tobacco (Bunsen and Kirchhoff). It has been found especially in the leaves of many plants, in cacao, coffee, and sugar-cane. It appears however that lithium salts cannot replace potassium salts in plants; indeed, when added in quantity they generally seem to act as a poison. In certain plants, however, such as for instance the *Samolus Valerandi*, lithium appears to act beneficially, inasmuch as the stronger plants contain most lithium.

From the vegetable world lithium finds its way into the animal kingdom; thus Bunsen and Kirchhoff observed its

[1] *Phil. Mag.* 1860 (4), **20**, 97. [2] *Pogg. Ann.* 1825, **4**, 245.
[3] *On Thames Water.* A. and F. Dupré. *Phil. Mag.* 1860 (4), **20**, 373.
[4] *Jahresb.* 1861, 1091. [5] *Chem. News*, 1864, **10**, 181.
[6] *Ber.* 1874, **7**, 653; *Compt. Rend.* 1874, **78**, 1022.

presence in the ashes of milk and in human blood and muscular tissue. Nor is lithium a metal which is confined to terrestrial matter, for Bunsen[1] has detected it in two meteoric masses, one of which fell at Juvenas in France on May 15, 1821, and the other at Parnallee in Southern India on 28th February, 1857, and Engelbach[2] observed lithium in a meteorite from the Cape. The presence of lithium in the atmosphere of the sun is at present doubtful.

130 *Extraction of Lithium Salts.*—1. From petalite and lepidolite. The first method of extraction, proposed by Berzelius,[3] consists in fusing the powdered mineral with double its weight of lime. On dissolving the fused mass in hydrochloric acid, and evaporating with sulphuric acid, the lithium is obtained in solution as sulphate, together with some aluminium sulphate and gypsum. The first salt is precipitated by addition of chalk, and the second by oxalate of ammonium. This method was improved by Regnault and again much simplified by Troost.[4] This latter chemist fuses the following mixture at a very high temperature in a wind furnace: finely powdered lepidolite, 10 parts; barium carbonate, 10 parts; barium sulphate, 5 parts; potassium sulphate, 3 parts. The heavy silicate and sulphate of barium sink to the bottom, and a layer of the sulphates of potassium and lithium is found at the top of the fused mass. These can be extracted by simple lixiviation. The sulphates are then converted into chlorides by the addition of barium chloride, the chlorides evaporated to dryness, and the lithium chloride extracted by treatment with a mixture of absolute alcohol and ether.

2. For the purpose of extracting lithium salts from triphyline, a process proposed by Hugo Müller[5] is the best. This consists in dissolving the mineral in hydrochloric acid, oxidising with nitric acid, precipitating the phosphoric acid with a ferric salt, evaporating to dryness and extracting with hot water. Chlorides of manganese and lithium are thus dissolved. The manganese is precipitated by sulphide of barium, and the excess of barium removed by sulphuric acid. The oxalate of lithium is obtained by evaporating with oxalic acid, and this on ignition is converted into the carbonate.

131 *Preparation of Lithium.*—The attempts made by Arfved-

[1] *Annalen*, 1861, **120**, 253.
[2] *Pogg. Ann.* 1862, **116**, 512.
[3] *Traité*, **2**, 89.
[4] *Compt. Rend.* 1856, **43**, 921.
[5] *Annalen*, 1853, **85**, 251.

son and Gmelin to prepare metallic lithium were fruitless. They endeavoured to separate the metal by the electrolysis of its salts but the battery they used was not powerful enough. Later on, the decomposition of lithia was tried by heating it with iron, and carbon; these experiments also proved abortive. Then Davy succeeded in obtaining a small quantity of the metal by electrolysis, but was unable to examine its properties. In 1858 Bunsen and Matthiessen were the first to obtain lithium by electrolysis in quantity, and to examine its properties carefully. The following is Bunsen's description of the process:[1] "Pure chloride of lithium is fused over a Berzelius' spirit-lamp (or Bunsen's gas-lamp), in a small thick porcelain crucible, and is decomposed by a zinc-carbon battery consisting of four to six cells. The positive pole is a small splinter of gas-coke, and the negative an iron wire about the thinness of a knitting-needle. After a few seconds, a small silver-white regulus is formed under the fused chloride round the iron wire and adhering to it, which after two or three minutes attains the size of a small pea: to obtain the metal, the wire pole and the regulus are lifted out of the fused mass by a small flat spoon-shaped iron spatula. The wire can then be withdrawn from the still melted metal, which is protected from ignition by the chloride of lithium with which it is coated. The metal may now be easily taken off the spatula with a pen-knife, after having been cooled under rock oil. As this operation can be repeated every three minutes, an ounce of chloride of lithium may be reduced in a very short time."

Lithium cannot be obtained by a similar process to that by which sodium and potassium are prepared by heating the carbonate with charcoal, or by heating the hydroxide with iron, as it can only be volatilised in a current of hydrogen at a white heat (Troost).

Properties.—Lithium is a solid, possessing a silver-like lustre, but tarnishes on exposure to the air. It is much less oxidisable than potassium or sodium. It is not so soft as these metals, but is softer than lead, and makes a grey streak on paper. Lithium can be pressed into wire, and can be welded at ordinary temperatures. It melts at 180°, and if the melted metal be pressed between two sheets of glass, a surface is obtained which exhibits the colour and brilliancy of polished silver. Lithium floats on

[1] *Journ. Chem. Soc.* 1856, 143.

petroleum, and is the lightest of all known solids, its specific gravity varying from 0·5891 to 0·5983 (Bunsen).

Heated in the air lithium ignites at a temperature above its fusing point, burning tranquilly with a bright white light. It also burns when heated in hydrogen, chlorine, bromine, iodine, dry carbon dioxide, or sulphur vapour, and combines readily with nitrogen on heating and slowly absorbs the gas even at the ordinary temperature forming the nitride. When thrown on to water it oxidises, but does not fuse like sodium. Nitric acid acts on it so violently, that it fuses and often ignites. Concentrated sulphuric acid attacks it slowly, but dilute sulphuric and hydrochloric acids quickly. Silica, glass, and porcelain are attacked by lithium at a temperature below 200° (Bunsen and Matthiessen). Lithium is more electro-negative than sodium.

COMPOUNDS OF LITHIUM.

Lithium and Oxygen.

132 *Lithium Oxide*, Li_2O.—Dry oxygen does not act upon lithium at the ordinary temperature. Indeed the metal may be melted in the air without losing its brilliancy. Heated much above 180° lithium takes fire and burns brilliantly in the air with the formation of lithium oxide or lithia which is coloured yellow by a small quantity of a higher oxide. It may be prepared in a purer state by heating nitrate of lithium in a silver basin. It forms a white crystalline mass which dissolves slowly in water with the formation of the hydrate, LiOH. This latter compound is also obtained by boiling carbonate of lithium for some hours with milk of lime, and evaporating the clear liquid to dryness in a silver basin. It forms a white caustic crystalline mass resembling caustic soda, which melts at a red-heat, does not volatilise at a white heat, and is insoluble in a mixture of alcohol and ether. Its solution absorbs carbonic acid from the air but less rapidly than soda does and it does not deliquesce on exposure. Crystalline hydrates $LiOH + H_2O$ and $2LiOH + H_2O$ have been obtained.[1]

[1] Muretow, *Ber.* 1872, **5**, 331; Göttig, *Ber.* 1887, **20**, 2912.

Lithium and Hydrogen.

Lithium Hydride $(LiH)_n$.—Lithium slowly combines with hydrogen at a dull red-heat, and rapidly at a bright red-heat with incandescence, forming the white solid hydride. The latter is only slowly altered in the air, and is decomposed by water with evolution of hydrogen and formation of the hydroxide.[1]

Salts of Lithium.

133 Many of the salts of lithium are isomorphous with those of sodium and silver, whilst in the alums this element can replace potassium and the other alkali metals. Lithium differs in a marked manner from sodium, potassium, &c., by forming a sparingly soluble carbonate and phosphate.

Lithium Chloride, LiCl.—This salt is formed when lithium burns in chlorine, or when lithia or the carbonate is dissolved in hydrochloric acid. Its preparation from spodumene and petalite has already been described. By evaporating the aqueous solution above 15°·5, or the alcoholic solution over sulphuric acid, the chloride is obtained in octohedra. The salt has a specific gravity of 2·074, and melts at a low red-heat to a mobile liquid; it is one of the most deliquescent salts known, and is also very soluble in alcohol. When its aqueous solution is evaporated to dryness, traces of hydrochloric acid are given off, a little lithia being formed, and on re-dissolving, the liquid has an alkaline reaction. Three hydrated chlorides are known, viz., $LiCl + H_2O$, $LiCl + 2H_2O$ and $2LiCl + 3H_2O$.

100 parts of water dissolve:

At	0°	20°	65°	80°	140°	160°
LiCl	63·7	80·7	104·2	115	139	145 parts

The saturated solution boils at 171° (Kremers).

Lithium iodotetrachloride, $LiICl_4 + 4H_2O$, is obtained by the action of chlorine on a solution of lithium chloride and iodine in dilute hydrochloric acid and crystallises in needles.[2]

Lithium sulphate, $Li_2SO_4 + H_2O$, is obtained by dissolving the

[1] Guntz, *Compt. Rend.* 1896, **122**, 244.

[2] Wells and Wheeler, *Zeit. Anorg. Chem.* 1891, **2**, 255.

carbonate in dilute sulphuric acid, and crystallises in thin monosymmetric plates, which dissolve readily in water and alcohol. The *acid sulphate*, $LiHSO_4$, is also known.[1]

Lithium potassium sulphate, $LiKSO_4$, separates out in hexagonal crystals when a hot solution of the two sulphates in equal molecular proportions is allowed to cool.

Lithium nitrate, $LiNO_3$, is prepared by dissolving the carbonate in nitric acid, and is very soluble in water and alcohol. It crystallises in anhydrous rhombohedra isomorphous with sodium nitrate (Troost); at 18° long prisms containing 3 molecules of water separate out.[2]

Normal Lithium Phosphate, Li_3PO_4, is distinguished from the phosphates of the other alkali metals by its slight solubility in water, in this respect resembling the phosphates of the next group of metals. It is precipitated as a crystalline powder by adding a lithium salt to common sodium phosphate together with caustic soda. It may also be obtained as a light amorphous powder by treating a lithium salt of a volatile acid with an excess of sodium phosphate. It dissolves in 2,539 parts of water and in 3,920 of water rendered alkaline by ammonia. In presence of ammoniacal salts it is much more soluble, and is precipitated from the solution by heating with caustic potash. It is readily soluble in hydrochloric and nitric acids; baryta water precipitates the phosphoric acid from the solution as barium phosphate, the whole of the lithium salt remaining in solution (W. Mayer). When a nitric acid solution of the normal salt is evaporated and the excess of free acid driven off, the di-hydrogen salt, LiH_2PO_4, remains behind. This is readily soluble, and, on evaporation over sulphuric acid, deposits deliquescent crystals.

Normal Lithium Carbonate, Li_2CO_3.—This salt, unlike the carbonates of the other alkali metals, is but slightly soluble in water, thus more nearly resembling the carbonates of the next group of metals. It is precipitated as a crystalline powder when a concentrated solution of lithium chloride is poured into a solution of ammonium carbonate in aqueous ammonia, and the mixture heated so long as the precipitate increases in bulk.

100 parts of water dissolve at:

0°	10°	20°	50°	75°	100°
1·539	1·406	1·329	1·181	0·866	0·728

[1] Schultz, *Pogg. Ann.* 1868, **133**, 137. [2] Dott, *Pharm. Journ.* **53**, 215.

parts of lithium carbonate, whilst at 102° the numbers 0·796 and 0·995 were obtained when the solution had boiled for 15 and 60 minutes respectively.[1]

If the solution be slowly evaporated crystalline crusts or small transparent crystals of the salt separate out, and if these be suspended in water and carbon dioxide passed in, *lithium hydrogen carbonate*, $LiHCO_3$, is formed. On evaporation the solution loses carbon dioxide again depositing the normal salt. Lithium carbonate is employed in medicine, especially in gouty affections, as it acts as a solvent for uric acid.

Lithium orthosilicate, Li_4SiO_4, is prepared by fusing lithium carbonate with the requisite quantity of silica, and crystallises in the same form as olivin, whilst the *metasilicate*, Li_2SiO_3, has the same form as hypersthene. Both salts are partly decomposed by water.

Detection and Estimation of Lithium.

134 The presence of extremely small traces of lithium compounds ($\frac{9}{10000000}$ of a milligram) can be ascertained with certainty by means of the spectroscope. The luminous vapour of lithium, obtained by bringing a trace of the salt on a fine platinum wire into the non-luminous gas flame, gives, when examined by a spectroscope, two sharply-defined lines—the one a very weak yellow line, Liβ (wave-length = 6104); the other a bright red line Liα (wave-length = 6708). Not only do all the lithium salts when thus heated give this reaction, but ashes of plants and the lithium minerals only require for this purpose to be held in the flame. Natural silicates which only contain traces of lithium must first be subjected to the following treatment. A small portion of the substance is digested with hydrofluoric acid, the residue moistened with sulphuric acid and heated; the dry mass is then treated with alcohol and the extract allowed to evaporate in a shallow dish. The solid particles are scraped off and brought into the flame on the platinum wire (Bunsen).

Lithium is separated from all the heavy and earthy metals in the ordinary process of analysis. It may be separated from potassium by the precipitation of the latter metal as the insoluble double chloride of potassium and platinum, the

[1] Bewad, *Journ. Russ. Chem. Ges.* 1884, i. 591.

corresponding lithium compound being soluble. It can be separated from sodium by the solubility of lithium chloride in a mixture of ether and absolute alcohol. But as by this process a small quantity of sodium chloride is found to dissolve, it is best to determine the amount of chlorine in a given weight of the mixed chlorides, from which the quantities of lithium and sodium may be calculated.[1]

The atomic weight of lithium was first accurately determined by Mallet in 1856 and 1859, and by K. Diehl in 1862. It was afterwards determined by Stas by converting the chloride into the nitrate, and by the determination of chlorine in lithium chloride, the atomic weight deduced from these numbers being 6·98 (O = 15·88).

RUBIDIUM, Rb = 84·8.

135 In the year 1860 Bunsen[2] announced the discovery by means of spectrum analysis of a new alkali metal, to which he gave the name of *Cæsium*, and in 1861 he discovered by the same method a second new alkali metal, and to this he gave the name *Rubidium*.

These two metals and their compounds possess so close a resemblance, and at the same time give reactions so similar to those of potassium, that they cannot be distinguished either from the well-known alkali or from one another by any of the common wet reactions or blowpipe tests. The only means by which their presence can be readily detected is by their spectrum reactions, and these are so delicate and so characteristic that they serve for the certain recognition of the minutest trace of these two new bodies, whether present alone or mixed with the other alkalis. The metals were first met with by Bunsen in the waters of Dürkheim in the Palatinate, and in the mineral petalite. In these, however, they are contained in such small quantity that, although their presence can be easily recognised in a few drops of the water or in a few grains of the mineral, it was requisite to boil down 40 tons of the water and to work up 150 kilograms of the mineral in order to obtain enough of the new metals to serve for the investigation of their compounds.

[1] Bunsen, *Phil. Mag.* 1862 (4), **24**, 48.
[2] *Berlin Acad. Ber.* May 10, 1860.

The following extract from Bunsen and Kirchhoff's second memoir on Spectrum Analysis[1] gives a clear idea of the method by which the presence of the two new metals was first detected :—

"If a drop of the mother-liquor of the Dürkheim water be brought into the flame of the spectrum apparatus, the characteristic lines of sodium, potassium, lithium, calcium, and strontium are at once seen. If the lime, strontia, and magnesia be separated according to well-known processes, and if the residual alkali bases in the form of nitrates be washed out with alcohol, and the lithium removed as completely as possible by precipitation with carbonate of ammonium, a mother-liquor is obtained which in the spectrum apparatus shows the lines of sodium, potassium, and lithium, but besides these, two splendid blue lines situated close together, and almost coinciding with the blue strontium line Srδ.

"As no known elementary body produces two blue lines in this portion of the spectrum, we may consider the existence of this hitherto unknown alkali element as thus placed beyond doubt.

"The facility with which a few thousandths of a milligram of this body may be recognised by the bright blue light of its incandescent vapour, even when mixed with large quantities of more common alkalis, has induced us to propose for it the name *Cæsium* (and the symbol Cs), derived from the Latin *cæsius*, used to designate the blue of the clear sky.[2]

"If Saxony lepidolite be treated by any of the known plans for separating the alkalis from the other constituents, and if the solution of the alkalis thus obtained be precipitated with dichloride of platinum, an abundant precipitate is formed, which, when examined in the spectrum apparatus, shows only the bright potassium lines. If this precipitate be repeatedly washed with boiling water, and the residual salt occasionally examined in the apparatus, two splendid violet lines lying between the strontium line Srδ and the blue potassium line Kβ will be noticed on the gradually fading continuous background of the potassium spectrum. These new lines increase in brilliancy as the washing is continued, and a number more appear in the red, yellow, and green portions of the spectrum.

[1] *Phil. Mag.* 1861 (4), **22**, 330.

[2] Aulus Gellius, in his *Noctes Atticæ*, ii. 26, quotes Nigidius Figulus as follows: "Nostris autem veteribus cæsia dicta est, quæ a Græcis γλαυκῶπις ut Nigidius ait, de colore cœli quasi cœlia."

"None of these lines belong to any previously known body. Amongst them are two which are especially remarkable as lying beyond Fraunhofer's line A and the potassium line K*a* coincident with it, and therefore situated in the outermost portion of the red solar rays. Hence we propose for this new metal the name *Rubidium* (and the symbol Rb), from the Latin *rubidus*, which was used to express the darkest red colour."[1]

Since this discovery, rubidium has been shown to be widely distributed, generally accompanying the other alkalis, but in very minute quantities. Rubidium occurs in many minerals, such as lepidolites, and triphylines, in Stassfurt carnallite, in Vesuvian leucite, in the porphyrites of the Palatinate, in mica and in orthoclase.

The following is the analysis of the lepidolite from Rozena in Moravia in which Kirchhoff and Bunsen first discovered rubidium :—

Silica	50·32
Alumina	28·54
Ferric oxide	0·73
Lime	1·01
Magnesia	0·51
Rubidium oxide	0·24
Cæsium oxide	trace
Lithium oxide	0·70
Lithium fluoride	0·99
Sodium fluoride	1·77
Potassium fluoride	12·06
Water	3·12
	99·99

A large number of brine-springs and mineral waters also contain the new alkali. Thus the hot springs of the Ungemach contain in 1 liter 1·3 milligram of chloride of rubidium (Bunsen); the mineral water of Bourbonne-les-Bains contains 18·7 milligrams of the same salt, and 32·5 milligrams of cæsium chloride.

The celebrated waters of Ems, Kissingen, Nauheim, Selters,

[1] Aulus Gellius, *Noctes Atticæ*, ii. 26. "Rubidius autem est rufus atrior et nigrore multo inustus."

Vichy; Wildbad-Gastein, and many others contain rubidium, and some of them also cæsium compounds. Rubidium has been found in sea-weed and in sea-water (Sonstadt),[1] and also in the mother-liquors (bitterns) from the salterns of Villefranche (Grandeau). Rubidium salts are also widely met with in the vegetable kingdom. Beetroot takes up these salts from the soil, and in the saline residue obtained by calcining the fermented molasses considerable quantities of rubidium salts are contained. Thus 100 parts of the saline residue contain 0·18 parts of chloride of rubidium (Grandeau). It has also been found in samples of tobacco grown in the most distant quarters of the globe—such as Algiers, Havana, Kentucky, France, and Macedonia. Rubidium likewise occurs in several kinds of coffee and tea (Grandeau); in the ash of the oak, *Quercus Pubescens*, in that of beech trees grown on a basaltic soil, in crude cream of tartar, in potashes from various sources and in crude carnallite. Plants can however not absorb rubidium salts in place of potassium salts, and they die if these latter are not present (Lucanus).

Mode of preparation of Rubidium compounds.—According to Bunsen the best source of rubidium is the saline residue left from the preparation of lithium salts from Saxon lepidolite. This consists of the chlorides of sodium, potassium, and lithium, and traces of the chlorides of cæsium and rubidium. The separation of these new metals is based upon the fact that their chlorides form double chlorides with platinic chloride, which are more insoluble than the corresponding potassium double chloride. One kilogram of the saline mixture is dissolved in 2·5 kilograms of water, and the cold liquid precipitated by a solution of thirty grams of platinum in aqua regia. The precipitate, having settled down, is collected and boiled twenty-five times successively with small quantities of water, in all about 1·5 kilograms, the liquid in each case being added to the solution of the original salt. A fresh precipitate is then formed, this is again washed and treated as the first, and when the above series of operations has been repeated seven or eight times the rubidium is found to be nearly all extracted. Each of the platinum precipitates is then dried, the platinum reduced by hydrogen, and the alkali chlorides dissolved in water. In this way 125 grams of rubidium chloride were obtained, containing three or four per cent. of chloride of potassium, and a

[1] *Chem. News*, 1870, **22**.

little chloride of cæsium. By a repetition of the precipitation and washing of the platinochloride this quantity of potassium impurity can be so completely removed that the well-known red potassium line (Kα) is not seen with a spectroscope when some of the salt is held in the flame (Bunsen).

Numerous other methods for the separation of rubidium and cæsium from potassium have been proposed; amongst these may be mentioned precipitation with stannic chloride,[1] which converts them into the sparingly soluble stannic chlorides, $2RbCl, SnCl_4$, and $2CsCl, SnCl_4$, and conversion into the alums, both of which are only slightly soluble in water, and still less so in a solution of potassium alum.[2]

To separate rubidium from cæsium advantage is taken of the different solubilities of these sparingly soluble salts of the two metals. The platinochlorides do not give good results, but the alums, $Rb_2Al_2(SO_4)_4+24H_2O$ and $Cs_2Al_2(SO_4)_4+24H_2O$, have been successfully employed, the former being about four times as soluble as the latter.[3] The *bitartrates*, $RbHC_4H_4O_6$ and $CsHC_4H_4O_6$, may also be used, the latter being the more soluble.[4]

The best method of separation is that of Godeffroy which consists in the addition of antimony trichloride to a solution of the chlorides in concentrated hydrochloric acid, when the double cæsium antimony chloride $3CsCl, 2SbCl_3$ is precipitated, but not the rubidium salt.[5] The pure rubidium salt may then be obtained from the filtrate by evaporating nearly to dryness, removing the antimony by sulphuretted hydrogen, redissolving the mixture in concentrated hydrochloric acid, and adding a solution of stannic chloride in the same liquid. Rubidium stannochloride $2RbCl, SnCl_4$ is then precipitated and is found to be free from cæsium.[6]

The double salts of the two metals obtained in this manner are treated with water and sulphuretted hydrogen to remove antimony or tin, the filtered solution containing pure rubidium or cæsium chloride.

Metallic rubidium is prepared in an analogous manner to

[1] Feit and Kubierschky, *Chem. Zeit.* **16**, 335.

[2] Redtenbacher, *J. pr. Chem.* 1865, **94**, 442; Setterberg, *Annalen*, 1882, **211**, 100.

[3] Redtenbacher, *loc. cit.* Godeffroy, *Annalen*, 1876, **181**, 176.

[4] Allen. *Amer. J. Sci.* (2), **34**, 367.

[5] *Ber.* 1874, **7**, 375, 1895, **8**, 9; *Annalen*, 1876, **181**, 176.

[6] Muthmann, *Ber.* 1894, **26**, 1019, 1425.

potassium by heating a mixture of the carbonate and charcoal (obtained by the ignition of the bitartrate) to whiteness in an iron tube, and is also obtained by heating the carbonate or hydroxide with magnesium,[1] or the hydroxide with aluminium, rubidium aluminate being then also formed.[2]

It is a silver white metal of specific gravity 1·52, which at −10° is still soft and wax-like, melts at 38°·5, and emits at incipient redness a blue coloured vapour. Like potassium, it appears to form an explosive compound with carbon monoxide.

Rubidium Oxide and Hydroxide, Rb_2O and RbOH.—Rubidium on exposure to air at once becomes covered with a bluish coating of suboxide, and takes fire spontaneously more readily than potassium with formation of the white oxide, Rb_2O (Bunsen).

When thrown on to water rubidium burns like potassium. The *hydroxide* is best prepared by adding baryta-water to a solution of rubidium sulphate. It forms a greyish white, deliquescent mass, melts at a red-heat and is volatile in the flame of a Bunsen burner.

SALTS OF RUBIDIUM.

136 These salts present the greatest similarity to those of potassium and are isomorphous with them.

Rubidium Chloride, RbCl.—Rubidium takes fire in chlorine gas burning with a bright light. Chloride of rubidium crystallises in glittering cubes which melt at a red-heat. 100 parts of water dissolve 76·38 parts of the salt at 1°, and 82·89 parts at 7°.

The bromide and iodide are very similar to the corresponding potassium salts.

The rubidium haloids unite with a large number of metallic chlorides forming double salts which for the most part crystallise well. Rubidium also forms compounds containing a larger number of halogen atoms much more readily than potassium, the compounds being also more stable. The following are known and are all crystalline; $RbBr_3$, $RbClBr_2$, $RbCl_2Br$, RbI_3, $RbBr_2I$, $RbCl_2I$, RbClBrI, $RbCl_4I$.[3]

[1] *Ber.* 1890, **23**, 51. [2] Beketoff, *J. Russ. Chem. Ges.* 1888, 363.
[3] *Amer. J. Sci.* (3), **46**, 88, 269; *Amer. J. Sci.* (3), **43**, 475, **44**, 42.

Rubidium Chlorate, $RbClO_3$, is obtained by the double decomposition of rubidium sulphate and barium chlorate. It crystallises in small prisms which taste like potassium chlorate, and of which 2·8 parts dissolve in 100 parts of water at 4°·7 and 5·1 parts at 19°.

Rubidium Perchlorate, $RbClO_4$, is a granular powder consisting of glittering microscopic crystals belonging to the rhombic system. When heated below redness it decomposes into rubidium chloride and oxygen. 100 parts of water dissolve 1·085 parts of the salt at 21°·3.

Normal Rubidium Sulphate, Rb_2SO_4, exists as large rhombic crystals which taste like potassium sulphate. 100 parts of water dissolve 42·4 parts of this salt at 10°.

Rubidium Nitrate, $RbNO_3$, crystallises in needles or prisms, and is very soluble in water; 100 parts of water dissolve at 0° 20·1, and at 10° 435 parts of this salt. It can be distinguished from nitre, inasmuch as it readily dissolves in concentrated nitric acid.

Rubidium Carbonate, Rb_2CO_3.—The normal salt is obtained by decomposing the sulphate with baryta water and evaporating the filtrate with ammonium carbonate. It is a deliquescent powder which is very soluble in water. If the solution of this salt be saturated with carbon dioxide, and allowed to evaporate over sulphuric acid, glittering prisms of the acid salt, $HRbCO_3$, are obtained; these have a cooling taste and are easily soluble in water.

Detection and Estimation of Rubidium.

137 The rubidium salts when brought into the non-luminous gas flame impart to it a tint of a rather more red shade than is produced by the potassium salts.

The flame spectrum exhibits two characteristic lines in the violet Rbα (wave-length 4202) and Rbβ. These are the most valuable as the means of recognising the rubidium salts. Two other rubidium lines, Rbδ (7950) and Rbγ (7811), are seen at the red end of the spectrum; they are both less refrangible than the red potassium lines. Besides these several other characteristic lines occur. The spectrum reaction for rubidium is so delicate that 0·002 mgrm. can be readily detected (Bunsen).

Bunsen determined the atomic weight of the metal by precipitating the pure chloride by nitrate of silver. He found as

a mean result the number 84·8 (O = 15·88) for the atomic weight of rubidium, and Grandeau obtained a closely corresponding number by the analysis of the sulphate, the same number being also found by Godeffroy.

CÆSIUM, Cs = 131·9.

138 This metal is remarkable not only as having been the first one discovered by spectrum analysis, but also because even before Bunsen's discovery of this metal, chemists had investigated certain cæsium compounds, which however they had mistaken for potassium salts. Thus, in the year 1846, Plattner analysed a rare mineral found in the island of Elba, and termed Pollux,[1] with the following result:—

Silica	46·20
Alumina	16·39
Ferric oxide	0·86
Potash	16·51
Soda	10·47
Water	2·32
	92·75

Plattner, being a careful experimentalist, sought for an explanation of the fact that his analyses did not add up to 100 parts, although he searched in vain for all other constituents. The explanation of the enigma was given by the discovery of cæsium, for Pisani,[2] in the year 1864, found on analysis of another sample of the same mineral that the alkali which Plattner had mistaken for potassium is, in reality, cæsium. His analysis gave the following numbers:—

Silica	44·03
Alumina	15·97
Ferric Oxide	0·68
Lime	0·68
Cæsia	34·07
Soda	3·88
Water	2·40
	101·71

[1] *Pogg. Ann.* 1846, **69**, 443. [2] *Compt. Rend.* 1865 **60**, 714.

If we now calculate the quantity of cæsium oxide corresponding to the amount of potash found by Plattner as the platinum double salt, we obtain the number 35·69; if we next subtract the weight of the chloride of cæsium thus found from the weight of the mixed chlorides of cæsium and sodium as found by Plattner, we obtain the number 1·72 as the amount of soda present. These numbers correspond satisfactorily with Pisani's results, especially when we remember that the quantity of mineral analysed by Plattner was very small. Both analyses, therefore, lead to the formula for pollux of—

$$10SiO_2 + 5(Cs_2O, Na_2O, CaO) + 2(Al_2O_3, Fe_2O_3) + 2H_2O.$$

It has already been mentioned under rubidium that cæsium occurs generally together with this and the other alkali metals. Cæsium alone is found in the mineral waters of Frankhausen, of Monte Latino in Tuscany, as well as in the Wheal Clifford Spring, one liter of this latter water containing 1·71 mgrms. of cæsium chloride (Yorke). It is a remarkable fact that plants do not take up any cæsium compounds from the soil, and in absence of potassium compounds, cæsium acts as a poison upon vegetable life (Lucanus). The sources from which cæsium is derived, and its separation from other metals and finally from rubidium, have already been described under the latter metal.

Cæsium was obtained by Setterberg by the electrolysis of a mixture of cæsium and barium cyanides, and by Beketoff by heating cæsium hydroxide with aluminium to a bright red heat in a nickel retort. The metal is of a silver-white colour, takes fire when heated in the air, melts at 26·5°, and has a specific gravity of 1·88 at 15°.[1] In the presence of mercury an amalgam is formed which is more electro-positive than the rubidium amalgam, and hence metallic cæsium is the most electro-positive of the metals.

Cæsium Hydroxide, CsOH, is obtained by a process similar to that by which rubidium hydroxide is prepared, and resembles it in every particular.

[1] Setterberg, *Annalen*, 1882, **211**, 100.

SALTS OF CÆSIUM.

139 The cæsium salts are isomorphous with those of potassium and rubidium. They colour the flame of a still more reddish tint than the salts of the last named metal.

Cæsium Chloride, CsCl, crystallises in small cubes which melt at a dull red heat, and volatilise even more readily than potassium chloride. It is very hygroscopic and deliquesces in moist air. The *bromide* and *iodide* are similar to the corresponding potassium salts. Like the rubidium haloids, the cæsium derivatives form a very large number of well crystallised double salts with other metallic haloids. A number of polyhaloid salts are also known, most of which are crystalline : among these may be mentioned $CsBr_3$, $CsBr_5$, CsI_3, CsI_5 and $CsCl_4I$ (Wells, Penfield, and Wheeler).

Normal Cæsium Sulphate, Cs_2SO_4, forms short, hard, prismatic crystals, insoluble in alcohol though readily soluble in water. The acid salt, $HCsSO_4$, crystallises in rhombic prisms.

Cæsium Nitrate, $CsNO_3$, crystallises in small glittering prisms which possess the cooling taste of saltpetre, and are slightly soluble in alcohol. 100 parts of water at 3°·2 dissolve 10·58 parts of this salt.

Normal Cæsium Carbonate, Cs_2CO_3.—This salt separates out from a syrupy solution in the form of ill-defined hydrated deliquescent crystals. They melt on heating, leaving a residue of the anhydrous salt as a sandy powder. It is soluble in absolute alcohol. 100 parts of alcohol dissolve at 19° 11·1, and at the boiling point 20·1 parts of the anhydrous salt. The acid salt, $CsHCO_3$, crystallises from aqueous solution in large prisms.

Detection and Estimation of Cæsium.

The spectrum of cæsium contains in addition to the two characteristic bright blue lines Csα and Csβ (4555 and 4593), several other less distinct lines.

The atomic weight of cæsium has been ascertained by the analysis of the chloride by means of silver nitrate. Johnson and Allen as well as Bunsen thus obtained the number 132·0 whilst Godeffroy obtained the number 131·6, giving an average of 131·8.

AMMONIUM COMPOUNDS.

140 The name *volatile alkali* was long ago given to ammonia as pointing out its similarity to the fixed alkalis potash and soda. In 1808, Seebeck made the interesting discovery that when mercury is brought into a strong aqueous solution of ammonia, and an electric current is passed through it, the metal increases rapidly in bulk, giving rise to an amalgam-like mass. The same observation was made almost simultaneously by Berzelius and Pontin, whilst Davy, as soon as he was informed of the fact, repeated the experiment and discovered that a piece of sal-ammoniac moistened with water might be employed instead of aqueous ammonia. Davy also noticed that the same amalgam-like mass is formed when an amalgam of potassium is thrown into a concentrated solution of sal-ammoniac. Hence he, like Berzelius, came to the conclusion that ammonia must contain oxygen, and that in this experiment, it, like potash and soda, had been reduced by the electricity to a metal-like body. To this metal-like substance, which was supposed to exist in this amalgam, they gave the name of *ammonium*. This view of the constitution of the ammonium compounds was objected to by Gay-Lussac and Thénard, who, from their experiments on the subject, carried out in the year 1809, concluded that the formation of the amalgam is due to a combination of the ammonia with hydrogen. They arrived at this result from observing that the amalgam undergoes rapid spontaneous decomposition into mercury, ammonia, and hydrogen gas. Arguing from analogy, the French philosophers were inclined to believe that in like manner potassium and sodium could not be considered to be true metals, but were rather the hydrogen compounds of the alkalis. In reply to these objections, Davy and Berzelius showed that the hydrogen which was evolved might arise from the decomposing action of the metallic ammonium upon the water which adhered to it, in the same way as hydrogen is evolved when sodium and potassium are thrown into water. Berzelius continued for many years to hold the view that oxygen is contained in ammonia, and he explained the fact that this element could not be detected in the ammonia, by assuming that nitrogen itself is an oxide of an element hitherto not isolated, to which he gave the name of *nitricum*.

Ampère was the first, in the year 1816, to endeavour to explain the analogy of the ammoniacal salts with those of the fixed alkalis. He showed that the differences in composition between the salts of a fixed and those of the volatile alkali disappear when we assume that, in the latter class of salts, a compound radical exists composed of one volume of nitrogen to four volumes of hydrogen; so that sal-ammoniac or hydrochloride of ammonia may be regarded as the chloride of a metal-like substance to which the name of ammonium had been given. In 1820, Berzelius gave up his old view and accepted the ammonium theory. He showed that aqueous ammonia must be regarded as a solution of ammonium oxide, and assumed that when anhydrous ammonia unites with a hydrogen acid (a substance to which we now give the simple name of acid) the ammonia combines with the hydrogen of the acid to form the metal-like radical ammonium, and that this becomes an oxide by union with the oxygen of the water.

According to our present views the ammonium salts are considered as being derived from acids by the replacement of their hydrogen by the radical ammonium. These salts are isomorphous with the salts of potassium, and otherwise exhibit a close analogy with them, as also with those of rubidium and cæsium.

Ammonium Amalgam.—This substance, whose existence has already been mentioned, is formed when a piece of moistened sal-ammoniac is laid on a platinum basin, a small quantity of mercury poured upon it, and this brought in contact with the negative pole of an electric battery, the positive pole being connected with the platinum basin. It may be obtained, still more readily, by throwing sodium amalgam containing 1 per cent. of sodium into a concentrated solution of sal-ammoniac. The mercury increases in bulk to upwards of twenty times its original volume. It then contains from 0·6 to 0·9 per cent. of its weight of ammonium. This amalgam forms a light, soft, buttery mass which at low temperatures becomes crystalline and decomposes, even at $-29°$, with evolution of two volumes of ammonia and one volume of hydrogen. It may be distinguished from the amalgams of the alkali metals inasmuch as it does not reduce the salts of silver and copper.[1] Hence some chemists have supposed that it must be regarded merely as a solution of ammonia and hydrogen in mercury or as a metallic

[1] Landolt, *Annalen*, 1868, Suppl. **6**, 342.

froth. Against this view, however, it is to be remembered that neither of these gases, either alone or when mixed together, dissolves at all in mercury. Moreover the effect of the amalgam on the magnitude of polarisation of a battery is quite comparable with that of the amalgams of the alkali metals.[1]

Potassammonium and Sodammonium.—When metallic potassium or sodium is added to liquid ammonia, solution takes place and when the excess of ammonia is allowed to evaporate, a copper-coloured mass remains which has the composition NH_3K or NH_3Na. The determination of the molecular weight in solution renders it probable that these formulæ must be doubled, in which case they may be regarded as derivatives of the hypothetical diammonium NH_4—NH_4, having the constitution KNH_3—NH_3K and $NaNH_3$—NH_3Na respectively.

The solution of potassammonium in ammonia yields with oxygen, according to Joannis,[2] the oxides K_2O_2, K_2O_3, and K_2O_4 successively, whilst with carbon monoxide it yields the white explosive compound $K_2C_2O_2$ and with nitric oxide the hyponitrite $K_2N_2O_2$. Sodammonium yields similar compounds under like conditions, with carbonic oxide and nitric oxide, but with oxygen the first compound formed is *disodammonium hydroxide*, Na_2NH_2OH, which is a slightly pink substance, and dissolves in water without evolution of gas, but with great evolution of heat Further addition of oxygen causes the formation of Na_2O_3.

Ammonium and the Halogens.

141 *Ammonium Fluoride*, NH_4F, is obtained by saturating hydrofluoric acid with ammonia. The commercial hydrofluoric acid, however, generally contains lead and other metals which must be previously removed by the addition of a small quantity of ammonium carbonate and sulphide. The clear acid liquid is saturated with solid carbonate ammonium and then evaporated in a platinum basin. Ammonium fluoride crystallises in hexagonal tables or prisms. It has a sharp saline taste and deliquesces in moist air, is more easily soluble in water than sal-ammoniac, and decomposes at the ordinary temperature when in the moist state. It decomposes silicates on being heated

[1] Le Blanc, *Zeit. Phys. Chem.* 1890, **5**, 467.

[2] Joannis, *Compt. Rend.* 1889, **109**, 900; 1891, **112**, 392; 1891, **113**, 795; 1892, **115**, 820; 1893, **116**, 1370, 1518; 1894, **118**, 713.

with them with evolution of silicon tetrafluoride, and hence it is largely used in mineral analysis and for etching upon glass. This may be readily accomplished by allowing a solution of the salt to dry upon the place which it is desired to etch. It cannot be preserved in glass bottles but must be kept in vessels either of platinum, silver, or gutta-percha.

Hydrogen Ammonium Fluoride, NH_4F,HF, is formed when a solution of the normal salt is evaporated at a temperature of about 40°. It crystallises in colourless rhombic prisms which deliquesce slightly in the air and on heating evolve highly irritating and acrid fumes.

Ammonium Chloride, NH_4Cl.—The history of this salt, well known under the name of sal-ammoniac, has already been given in vol. i. p. 453. It is found in the fumeroles of Vesuvius, Etna, Hecla, and other volcanoes, as well as in the cracks and fissures in recent lava streams. Its formation has also been observed when large masses of coal undergo combustion, as when a coal pit is on fire. The salt has also been observed in guano from the Chincha Islands.

Sal-ammoniac originally served as the source from which all the ammoniacal salts were prepared. At present, however, they are usually obtained from ammonium sulphate, which is prepared from the ammoniacal liquor of the gasworks on an enormous scale. For the manufacture of the chloride the gas-liquor is distilled with lime in the manner described under ammonium sulphate, and the gaseous ammonia which is thus evolved together with sulphuretted hydrogen and carbon dioxide passed into hydrochloric acid of specific gravity 1·1 contained in a stone saturator, the ammonia being retained whilst the two last named impurities pass on unchanged. The solution is then evaporated to the crystallisation point, and the crude product purified by recrystallisation or more frequently by sublimation. The vessel employed for this purpose consists of two parts. The lower one is either a semi-circular earthenware vessel embedded in an iron one, or consists entirely of a cast-iron basin. The sal-ammoniac in the solid state is brought into this, and then a semi-circular dome-like cover, either of earthenware, lead, or iron, is placed over it, and this is luted tight with clay. In the centre of the dome there is an opening which is left open during the sublimation. Pure sal-ammoniac is also obtained by employing the same apparatus, but, instead of the impure salt, a mixture of common salt, NaCl, and ammonium sulphate,

$(NH_4)_2SO_4$, is heated, when sodium sulphate remains behind, sal-ammoniac subliming as before.

Pure ammonium chloride is colourless and odourless and has a sharp saline taste. It crystallises from a saturated solution in arborescent or feather-like growths which consist of an aggregation of small regular octohedra, and other forms of the regular system, as well as combinations of these, and often exhibit trapezohedric hemihedry, so that the crystals appear to belong to the hexagonal or quadratic system (Fig. 61). From a solution containing urea sal-ammoniac crystallises in cubes. When the salt is sublimed, and the vapour quickly cooled, it is precipitated in the form of a light crystalline powder known as flowers of sal-ammoniac. The common sublimed sal-ammoniac is a semi-transparent, fibrous, crystalline mass, which is so tough that it is difficult to powder the substance. For the purpose of obtaining it in a fine powder, a concentrated solution is evaporated down, and constantly stirred.

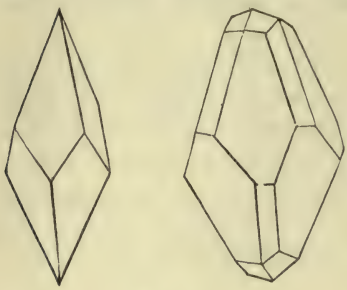


Fig. 61.

When sal-ammoniac dissolves in water a considerable reduction of temperature takes place; 30 parts of salt dissolve in 300 parts of water at 13·3° and the temperature is reduced to − 5°·1 (Rudorff). 100 parts of water dissolve at 0° 28·4, at 10° 32·8, and at 110° 77·2 parts of the salt;[1] the boiling point of the saturated solution is 115°. Sal-ammoniac is somewhat less soluble in alcohol; thus 100 parts of alcohol of specific gravity 0·939 dissolve at 8° 12·6, and at 56° 30·1 parts of the salt.[2] The specific gravity of sal-ammoniac is 1·52. It is not volatile at the ordinary temperature of the air, but when boiled with water ammonia escapes in small quantity, and the solution, which is at first perfectly neutral, becomes slightly acid. At higher temperatures it evaporates completely, giving rise to a colourless vapour, which, according to Bineau, has the specific gravity 0·89, corresponding to a vapour density of 13·345, whilst the molecular formula, NH_4Cl, requires a density of 26·69. From the fact of the abnormal density it has been argued that the sal-

[1] Alluard, *Annalen*, 1865, **133**, 292.

[2] Gerardin, *Ann. Chim. Phys.* 1865 [4], **5**, 129.

ammoniac vapour consists of a mixture of equal molecules of ammonia and hydrochloric acid. The truth of this supposition was first experimentally demonstrated by Pebal,[1] who allowed the vapour of sal-ammoniac to diffuse into an atmosphere of hydrogen, when the lighter ammonia was found to diffuse out and the heavier hydrochloric acid to remain behind. K. von Than [2] then showed that if dry ammonia and dry hydrochloric acid be brought together at a temperature of upwards of 350°, at which point sal-ammoniac is gaseous, no change either of temperature or of the volume of the gases is observed, whereas if chemical union had taken place a change of both these would naturally have been expected. Marignac [3] further observed that in the volatilisation of sal-ammoniac nearly the same amount of heat is absorbed as is evolved when ammonia and hydrochloric acid combine. It has also been shown that under diminished pressure and in an atmosphere of ammonia, the vapour density of ammonium chloride is 1·68—1·71, showing that under these conditions nearly the whole of the ammonium chloride volatilises without dissociation,[4] whilst if the ammonium chloride employed be absolutely dry it has the normal vapour density even under atmospheric pressure.[5]

This fact of the dissociation of sal-ammoniac can be readily shown by igniting a small piece of the solid in a closed platinum crucible. On removing the lid after the salt has been volatilised, and plunging a moistened piece of blue litmus paper into the crucible, the litmus paper will be turned bright red, proving the presence of free hydrochloric acid, the ammonia having escaped.

Sal-ammoniac is used in medicine. In former days that which came from Egypt was especially esteemed as a drug. Large quantities are used in the processes of dyeing, and workers in metal employ it in the processes of soldering and tinning, as at a high temperature it either reduces the metallic oxide or converts it into fusible chloride and thus gives rise to a bright metallic surface. It is also of value in the laboratory both as a reagent and as a convenient source of ammonia.

Ammonium Bromide, NH_4Br, is very soluble in water, and crystallises in white cubes which taste like sal-ammoniac.

Ammonium Iodide, NH_4I, is best obtained by saturating

[1] *Annalen*, 1862, **123**, 199. [2] *Annalen*, 1864, **131**, 129.
[3] *Compt. Rend.* 1869, **68**, 877. [4] Neuberg, *Ber.* 1891, **24**, 2543.
[5] H. B. Baker, *Journ. Chem. Soc.* 1894, i. 615.

ammonia with hydriodic acid. It crystallises in colourless cubes readily soluble in water and in alcohol. It deliquesces in moist air and gradually assumes a yellow colour due to the slow liberation of iodine. It is used in photography as it is soluble in alcohol.

When a small quantity of iodine is gradually added to a concentrated solution of ammonium nitrate, rendered alkaline by potash, ammonium di-iodide, NH_4I_2, separates out as a brownish black mobile liquid. This substance is soluble in alcohol and carbon bisulphide. Water decomposes it into iodide of nitrogen, NHI_2, ammonium iodide, and hydriodic acid:

$$4NH_4I_2 = NHI_2 + 3NH_4I + 3HI.$$

Ammonium Chlorate, NH_4ClO_3.—When ammonia is saturated with chloric acid and the solution evaporated, this salt crystallises out in small needles which have a strongly acrid taste and are very soluble in water and slightly soluble in absolute alcohol. Heated to 102° the salt decomposes (Wächter), chlorine, oxygen, nitrous oxide and aqueous vapour being evolved and sal-ammoniac remaining behind. Occasionally the salt undergoes spontaneous decomposition. When thrown on to a hot plate it decrepitates like ammonium nitrate.

Ammonium Perchlorate, NH_4ClO_4, is obtained by saturating ammonia with perchloric acid. It forms rhombic crystals which are isomorphous with potassium perchlorate and dissolve in five parts of cold water.

Ammonium and Sulphur.

142 The method of preparing volatile compounds of sulphur has long been known. Thus for instance, the writer who assumed the name of Basil Valentine states that a blood-red oil may be obtained by distilling together common sulphur, quicklime and sal-ammoniac. He also says, "Take grey sulphur and quicklime a pound, sal-ammoniac a fourth part; rub these together, when a splendid red oil is obtained, which fixes and refines." Beguin was also acquainted with this mode of preparation in the seventeenth century, and this salt was known as *spiritus sulphuris volatilis Beguinii*. Boyle in 1663 observed that the vapours of this body possess the power of blackening metals, and he therefore termed it a volatile tincture of sulphur,

and this same substance was known to the later chemists as *spiritus fumans Boylei*. This is a mixture of several sulphides of ammonia. Boerhaave in 1732 was the first to mention the fact that flowers of sulphur dissolve in ammonia, the substance thus obtained being known as volatile liver of sulphur. The preparation of the compound by leading sulphuretted hydrogen into ammonia was described by Kirwan in 1786.

Ammonium Sulphide, $(NH_4)_2S$, is obtained in colourless micaceous crystals by passing a mixture of sulphuretted hydrogen with a slight excess of ammonia into a vessel cooled to −18°, ammonium hydrosulphide being also formed as a porcelain-like mass. At the same time a very volatile liquid is condensed which has the composition $(NH_4)_2S,2NH_3$. Ammonium sulphide readily dissolves in water, but the properties of the solution render it probable that it is at the same time partially dissociated into ammonium hydrosulphide and ammonia.[1]

Ammonium Hydrosulphide, NH_4HS, is obtained by mixing sulphuretted hydrogen and ammonia in equal volumes at the ordinary temperature, and forms a porcelain-like mass; it is also formed if the sulphuretted hydrogen be present in slight excess, but is not the only product in presence of excess of ammonia. Its aqueous solution is obtained by saturating ordinary strong ammonia solution, diluted with four times its volume of water, with sulphuretted hydrogen, the strongest solution obtainable containing 16–19 per cent. of NH_4HS. If the solution of ammonia be more concentrated, compounds of the general formula $(NH_4)_2S,xNH_4HS$ are formed, the value of x decreasing step by step with the increase in the concentration of the solution. Thus with ammonia of specific gravity 0·880 the compound formed has the composition $(NH_4)_2S$, $2NH_4HS$, and separates, when the solution is cooled to 0°, in leaf-like crystals. Crystals having the composition $(NH_4)_2S,6NH_4HS$, $(NH_4)_2S$, $12NH_4HS$, and $(NH_4)_2S$, $18NH_4HS$ have also been prepared. The ammonium sulphide solution employed in the laboratory consists therefore of ammonium sulphide, hydrosulphide, and hydroxide in proportions varying with the concentration, and it also almost always contains a small quantity of polysulphides, which impart to it a yellow colour, these being formed by the action of the solution on the sulphur obtained from its partial oxidation.

Ammonium Polysulphides—Compounds containing more

[1] Bloxam, *Journ. Chem. Soc.* 1895, i. 283.

sulphur than the foregoing are obtained by the action of sulphur on solutions of ammonium sulphide; these were first examined by Fritsche, who described the tetrasulphide $(NH_4)_2S_4$, the pentasulphide, $(NH_4)_2S_5$, and the heptasulphide $(NH_4)_2S_7$, and regarded these as formed by the direct addition of sulphur to ammonium sulphide. The subject has been recently again investigated by Bloxam,[1] who has found that the formation of these compounds does not proceed in so simple a manner. The solution of ammonium sulphide, which as above mentioned usually contains the hydrosulphide, sulphide and free ammonia, acts on the sulphur with evolution of sulphuretted hydrogen and formation of two tetrammonium polysulphides, viz., the *enneasulphide* $(NH_4)_4S_9$ and the *heptasulphide* $(NH_4)_4S_7$, both of which crystallise in yellow needles, containing respectively seven and four molecules of water. These compounds by their decomposition give rise to the diammonium polysulphides, of which the following have been obtained in the crystalline form:

Ammonium tetrasulphide, $4(NH_4)_2S_4$, H_2O.
Ammonium pentasulphide, $(NH_4)_2S_5$, H_2O.
Ammonium heptasulphide, $3(NH_4)_2S_7$, $4H_2O$.
Ammonium enneasulphide, $2(NH_4)_2S_9$, H_2O, and $5(NH_4)_2S_9$, $4H_2O$.

143 *Normal Ammonium Sulphate*, $(NH_4)_2\,SO_4$. We find this salt mentioned by Libavius, but more accurately described by Glauber, who recommended its use as a medicine. It was long known by the name of *sal ammoniacum secretum Glauberi*. This salt is found in certain volcanic districts, especially in the neighbourhood of the boric acid fumeroles of Tuscany, and it is termed by mineralogists mascagnite. Ammonium sulphate is prepared on the large scale by heating the ammoniacal gas liquor with milk of lime and passing the ammonia evolved into sulphuric acid. The distillation is best carried out in a continuous still, the construction of which is analogous to the well-known Coffey still used in the distillation of alcohol. One of the best forms of still, viz., that devised by Feldmann,[2] is shown in Fig. 62. The ammoniacal liquor passes from the storage tank *a* into the supply tank *b*, and thence through the economiser J, where it is warmed by the hot waste gases coming from the saturator E. It flows thence into the top chamber of the column A, falls from

[1] *Journ. Chem. Soc.* 1895, i. 283.

[2] Patent No. 3643 (1882).

chamber to chamber by the overflow pipes *a*, and is subjected in each to a current of steam sub-divided into a number of small streams, which completely removes the whole of the volatile ammonia, *i.e.*, the ammonia present as sulphide and carbonate. In the chamber B it is mixed with milk of lime introduced by the pump G, and then passes into the top of the second column C where it is again subjected to

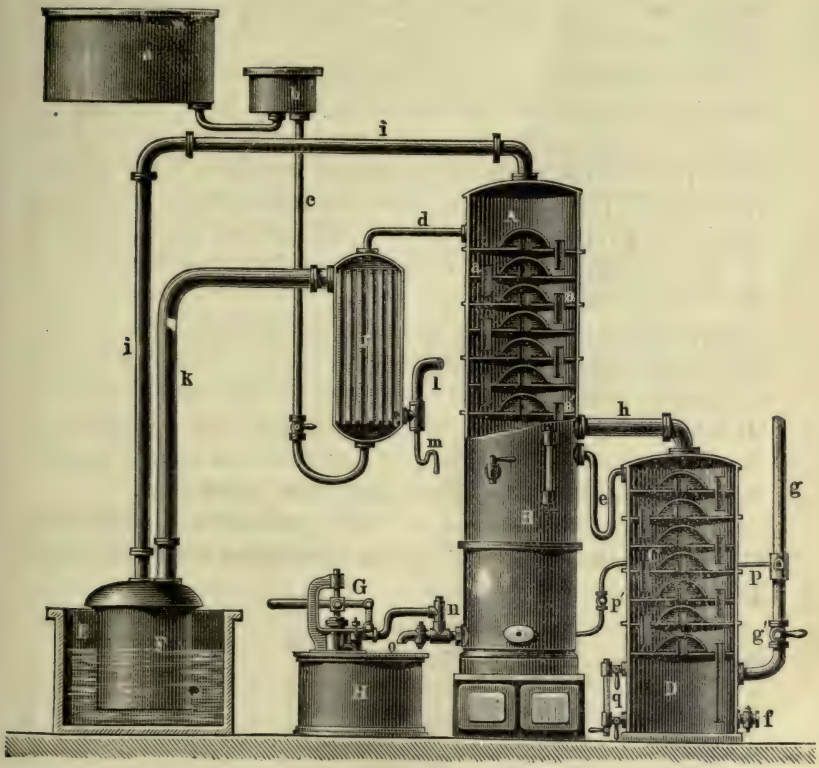


FIG. 62.

the action of the current of steam and freed from the fixed ammonia, *i.e.*, that present as sulphate, carbonate, &c., the acids remaining in combination with the lime. The waste liquor passes away from the bottom D, and is quite free from ammonia.

The steam required is introduced by the pipe *g* into the bottom of the column C, passes from the top to the bottom

of A, and leaves the latter, carrying with it the whole of the ammonia, sulphuretted hydrogen and carbon dioxide, by the pipe I, through which it is conveyed to the saturator E, which consists of an iron or wooden tank lined with lead and filled with sulphuric acid of 142° Tw. The latter absorbs the ammonia, forming ammonium sulphate, which is fished out as it separates and allowed to drain, the waste gases being retained within the bell F, and passing thence through the economiser J to another portion of the works where they are now usually treated for the recovery of sulphur.

The ammonium sulphate thus obtained is always slightly damp and contains a small quantity of free acid, but may be purified by recrystallisation. It forms large transparent crystals isomorphous with those of potassium sulphate, has a specific gravity of 1·77, and a sharp, bitter and saline taste. 100 parts dissolve at 0° 71 parts, and at 100° 97·5 parts of the salt, but it is only slightly soluble in aqueous alcohol and insoluble in absolute alcohol.

Ammonium sulphate is used for the manufacture of other ammonium salts, but its chief employment is as a nitrogenous manure, for which purpose it is used in immense quantities. Of late years, however, it has met with a serious competitor in the Chili saltpetre now so largely imported, and its sale has only been possible by making great reductions in the price.

The following table gives the total production of ammonium sulphate in the United Kingdom during the ten years, 1885–1894:

1885	97,000 tons.	1890	134,000 tons.
1886	106,500 „	1891	143,000 „
1887	113,700 „	1892	150,000 „
1888	122,800 „	1893	151,500 „
1889	133,000 „	1894	160,000 „

Ammonium Persulphate, $(NH_4)_2S_2O_8$.—This salt is obtained by the electrolysis of a solution of ammonium sulphate in dilute sulphuric acid, and crystallises in large prisms, which are very soluble in water.[1] It is now prepared on the manufacturing scale for use as an oxidising agent.

[1] Marshall, *Journ. Chem. Soc.* 1891, 777.

Ammonium and Nitrogen.

144 *Ammonium Azoimide* or *Ammonium Nitride*, N_4H_4 or $NH_4.N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.$ is formed by neutralising a solution of azoimide with ammonia, but is best obtained by saturating an alcoholic solution of diazohippuramide, $C_9H_8NO_2.NH.N:N.OH$, with ammonia gas; it crystallises in large lustrous prisms, which become opaque and slowly volatilise in the air, and on careful heating sublimes in small lustrous prisms. It is very soluble in water, has an alkaline reaction, and explodes with great violence when quickly heated.[1]

Ammonium Nitrite, NH_4NO_2, is best obtained by passing the nitrous fumes prepared by the action of nitric acid on arsenious oxide over ammonium carbonate kept cool by ice, the resulting mass being treated with alcohol, and precipitated with ether. It forms colourless deliquescent crystals which explode on heating to 60–70°, whilst in acid solution similar decompositions sometimes occur at the ordinary temperature.[2] The solution decomposes on heating with formation of nitrogen and water:

$$NH_4NO_2 = N_2 + 2H_2O.$$

Ammonium Nitrate, NH_4NO_3.—This salt was first prepared by Glauber and was originally known by the name of *nitrum flammans*. It crystallises when its solution is slowly evaporated, the crystalline form varying according to the temperature at which the crystallisation takes place; thus at 36° it crystallises in the asymmetric, at 87° in the hexagonal, and at 120° in the monosymmetric system. It has a specific gravity of 1·7, a strong saline taste, and dissolves at the ordinary temperature in half its weight of cold water, whilst it is still more soluble in hot water. When the salt is dissolved a considerable reduction of temperature takes place; thus if 60 parts of the salt be dissolved in 100 parts of water at a temperature of 13°·6 the temperature of the liquid sinks to − 13°·6, whilst if water at 0° be taken the temperature of − 16°·7 is obtained, this being the freezing point of the solution (Guthrie). It is also easily soluble in alcohol. When the dry salt is thrown on a red-hot plate it decomposes

[1] Curtius, *Ber.* 1891, **24**, 3348.
[2] Sorensen, *Zeit. Anorg. Chem.* 1894, **7**, 33.

with the evolution of a yellow flame and a slight explosion, into nitrogen, water, and nitric oxide, whereas if it be gently heated it decomposes into water and nitrous oxide, a small portion of the salt subliming unchanged. It is chiefly employed in the manufacture of nitrous oxide for anæsthetic purposes, and is also used for the preparation of freezing mixtures and as a constituent of certain explosives.

Ammonium and Phosphorus.

145 *Normal Ammonium Phosphate,* $(NH_4)_3PO_4$, is obtained as a crystalline semi-solid mass when hydrogen di-ammonium phosphate is supersaturated with concentrated aqueous ammonia. It crystallises from its solution in dilute ammonia in short prismatic needles. These contain three molecules of water of crystallisation and are moderately stable in the air, but on boiling the aqueous solution two-thirds of the ammonia is evolved.

Di-ammonium Hydrogen Phosphate, $(NH_4)_2HPO_4$, occurs in guano from Ichaboe (Herapath) and is easily formed when a solution of phosphoric acid containing an excess of ammonia is allowed to evaporate; transparent monosymmetric prisms are thus deposited.

Ammonium Di-hydrogen Phosphate, $(NH_4)H_2PO_4$, is formed when aqueous phosphoric acid is added to ammonia until the solution reddens litmus paper, and is no longer precipitated by barium chloride. It crystallises in quadratic prisms and is isomorphous with the corresponding potassium salt.

Hydrogen Ammonium Sodium Phosphate or *Microcosmic Salt,* $HNaNH_4PO_4 + 4H_2O$.—The old alchemists were aware that this peculiar salt can be obtained from urine, but Marggraf was the first to examine with care the salt which crystallises from evaporated urine and to show that it contains a volatile alkali, whilst Proust found in 1775 that sodium was contained in this compound. The salt was first termed *sal urinæ fixum* in contradistinction to the *sal urinæ volatile* or ammonium carbonate, but it was also termed *sal microcosmicum,* being obtained from the human body. This compound is also found in guano (Herapath).

In order to prepare the compound, five parts of common rhombic sodium phosphate are dissolved in hot water together with two parts of crystallised ammonium phosphate and the

solution allowed to cool. Transparent monosymmetric prismatic crystals separate out, having a specific gravity of 1·55 and possessing a strongly saline taste. They melt readily on heating, giving off water and ammonia and leaving a residue of the di-hydrogen sodium orthophosphate which again at a high temperature melts with loss of water, forming a clear liquid, and this on cooling yields a glassy mass of sodium hexametaphosphate. This substance is used largely as a blowpipe reagent.

Ammonium and Carbon.

146 *Carbonates of Ammonium.*—Commercial carbonate of ammonia, *sal-volatile*, or salt of hartshorn, forms the starting-point for these compounds. This substance was well known to the later alchemists who prepared it by the dry distillation of evaporated and decomposed urine, hartshorn, bones and other animal matters. Its preparation from sal-ammoniac was first described in the works attributed to Basil Valentine, but long after the 15th century it was supposed that the volatile alkaline salts obtained from various sources possessed different medicinal power. Even up to the end of the 17th century *English drops*, which were really nothing more than carbonate of ammonia mixed with an ethereal oil, were sold at high prices, and it was stated by some that the volatile alkali contained in this substance was prepared by the destructive distillation of silk, whilst others gave the remarkable receipt that five lbs. of skulls of persons who had been hanged or otherwise come to an unnatural end must be distilled with two lbs. of dried vipers, hartshorn, and ivory. More rational views concerning the composition of these compounds were arrived at towards the end of the 18th century. Dossie in his *Elaboratory laid Open*, published in 1758, distinctly states that the same animal substances always yield an equally efficacious kind of volatile alkali.

Commercial Carbonate of Ammonia, commonly known as the sesquicarbonate, is obtained by subliming a mixture of two parts of chalk and one part of sal-ammoniac or ammonium sulphate. This operation is conducted in iron retorts furnished with leaden receivers, and ten parts of sal-ammoniac yield from seven to eight parts of the carbonate. The salt is then resublimed with the addition of some water, and is thus obtained as a white semi-

transparent fibrous mass which has a strongly ammoniacal smell and a pungent caustic taste. This salt possesses the composition $N_3H_{11}C_2O_5$, and consists of a compound of hydrogen ammonium carbonate with ammonium carbamate (vol. i., p. 738); thus, $(NH_4)HCO_3 + NH_4CO_2NH_2$. By treating the salt with strong alcohol the carbamate can be dissolved whilst the ammonium bicarbonate remains undissolved. This same decomposition takes place when the salt is exposed to the air the carbamate undergoing slow volatilisation.

The impurities liable to occur in the commercial salt are thiosulphate, sulphate, and chloride of ammonium, lead from the receiver, and lime and calcium chloride from the chalk employed.

Normal Ammonium Carbonate, $(NH_4)_2\ CO_3 + H_2O$.—Dalton first prepared this salt by treating sal-volatile with a quantity of water insufficient to dissolve it completely. It is also obtained when ammonium carbamate is dissolved in water:

$$CO\begin{cases} NH_2 \\ ONH_4 \end{cases} + H_2O = CO\begin{cases} ONH_4 \\ ONH_4 \end{cases}$$

It is however most readily prepared by digesting the common commercial carbonate of ammonia for two hours at a temperature of 12° with strong aqueous ammonia and drying the crystalline powder which remains behind between blotting paper.

Transparent tabular or prismatic crystals are deposited from a solution prepared at a temperature of from 30° to 35°. These possess an ammoniacal odour, attract moisture from the air and become opaque from loss of ammonia and formation of hydrogen ammonium carbonate and water (Divers).[1]

Hydrogen Ammonium Carbonate or *Ammonium Bicarbonate*, $(NH_4)HCO_3$. Crystals of this salt are sometimes found in Patagonian guano and in the purifiers of gas-works. It is formed when the foregoing compound is allowed to lie exposed to the air, or when its solution is treated with carbon dioxide. It forms a white mealy powder, or, when slowly crystallised, large rhombic crystals, which have a cooling saline taste and do not smell of ammonia when in the dry state. At 60° it slowly undergoes decomposition with evolution of carbon dioxide, ammonia, and water. When it is more strongly heated in such a way that a small quantity of water condenses and the gases are not allowed to recombine, the ordi-

[1] *Journ. Chem. Soc.* 1870, 171.

nary commercial carbonate of ammonia is formed (Divers). This salt dissolves at 15° in 8 parts of water. Its solution when exposed to the air, as well as when heated above 36°, loses carbon dioxide, but its saturated solution can be crystallised by cooling out of contact with air. It is not soluble in alcohol, but if the alcoholic mixture be allowed to stand in the air carbon dioxide is evolved and normal ammonium carbonate dissolves. It forms a double salt with the former compound having the composition $2(NH_4)HCO_3 + (NH_4)_2CO_3 + H_2O$, which may be most easily obtained by treating the commercial salt at 30° with a moderate amount of tolerably concentrated ammonia and crystallising. This double salt forms flat rhombic prisms or thin six-sided tables, smells strongly of ammonia, and dissolves at 15° in 5 parts of water. It is decomposed by an excess of water with formation of the bicarbonate. Aqueous solutions of the carbonates are completely decomposed on boiling, the ammonia and carbon dioxide passing over with the steam.

147 *Ammonium Cyanide*, NH_4CN.—When a mixture of sal-ammoniac and dry ferrocyanide of potassium, or mercury cyanide, is heated, this salt sublimes in colourless cubes which smell of both ammonia and hydrocyanic acid. It is easily soluble in both water and alcohol and evaporates at a temperature of 36°. The vapour is inflammable and burns with a yellow flame. It is an extremely poisonous salt and decomposes, especially in the moist state, into azulmic acid.

Ammonium Cyanate, NH_4OCN, is formed when the vapour of cyanic acid is brought into contact with dry ammonia or by mixing concentrated solutions of potassium cyanate and ammonium sulphate. It forms a flocculent crystalline mass, easily soluble in water and sparingly soluble in absolute alcohol. This salt, as is well known, easily undergoes intramolecular change forming the isomeric urea $CO(NH_2)_2$ (vol. i. p. 738).

Ammonium Thiocyanate, NH_4CNS, is obtained by the dry distillation of organic substances containing nitrogen and sulphur, being probably formed as a secondary product due to the action of ammonia on carbon bisulphide; it is therefore found in appreciable quantity in gas-liquor. It is formed by warming a solution of yellow ammonium sulphide, which contains polysulphides, with hydrocyanic acid:[1]

$$(NH_4)_2S + HCN + S = NH_4CNS + NH_4HS;$$

[1] Liebig, *Annalen*, 1847, **61**, 126.

it is, however, most readily prepared by mixing together 600 grams 95 per cent. alcohol, 800 grams ammonia (specific gravity 0·912) and 350 to 400 grams carbon bisulphide, and allowing to stand for several days, then distilling off a portion of the liquid and allowing the remainder to crystallise.[1] Ammonium thiocarbonate, $(NH_4)_2CS_3$, is first formed in this reaction and on heating decomposes into the thiocyanate and sulphuretted hydrogen:

$$(NH_4)_2CS_3 = NH_4CNS + 2H_2S$$

It is very readily soluble in water and alcohol, crystallising out in colourless plates. Its solution in water is attended with great absorption of heat; thus if 100 grams of the salt be dissolved in an equal weight of water at 17°, the temperature sinks to −12° (Rüdorff). The perfectly dry salt melts at 159°, and when slowly melted is partially converted into the isomeric thio-urea $CS(NH_2)_2$ (vol. i. p. 746).

Hydroxylamine Salts.

148 *Hydroxylamine*, NH_2OH, the preparation of which has already been described (vol. i. p. 475), forms salts with acids which are analogous to those of ammonia; the most important of these are as follows:

Hydroxylamine Hydrochloride, NH_2OH,HCl, crystallises from a hot alcoholic solution in monosymmetric prisms or plates, which are very soluble in water but less so in alcohol. When heated it decomposes into ammonium chloride, hydrochloric acid, water and nitrogen. When a concentrated solution of this salt is treated with an alcoholic solution of hydroxylamine, it yields the salt $(NH_2OH)_2HCl$ as a crystalline precipitate, which when mixed with concentrated solutions of the normal salt yields large, well formed crystals having the composition $(NH_2OH)_32HCl$, and melting at 95° with decomposition.

Hydroxylamine Sulphate, $(NH_2OH)_2,H_2SO_4$, crystallises from aqueous solution in large monosymmetric prisms, according to v. Lang, or asymmetric prisms according to Dathe, and is precipitated in needles on addition of alcohol to the aqueous solution.

Hydroxylamine Nitrate, NH_2OH,HNO_3, is obtained by decom-

[1] Schultz, *J. pr. Chem.* 1883, (2), 27, 518.

posing a solution of the hydrochloride with silver nitrate or of the sulphate with barium nitrate. On evaporating the solution over sulphuric acid an oily liquid remains, which, when pure, forms crystals melting at 48°, and readily remains in superfusion. It is very readily soluble in water and alcohol, and its aqueous solution decomposes on the water bath with evolution of nitrous fumes.

Hydrazine Salts.

149 Hydrazine, N_2H_4, like ammonia, readily combines with acids to form salts, which may for convenience be described here, although they do not correspond to the ammonium salts and those of the alkalis, hydrazine being a di-acid base. The salts are for the most part obtained by neutralising hydrazine hydrate (vol. i. p. 471) with the acid whose salt is required, and evaporating the solution to the point of crystallisation.

Hydrazine Dihydrochloride, $N_2H_4,2HCl$, crystallises in regular octohedra, which rapidly attract moisture from the air. It melts at 198°, losing hydrogen chloride and forming the *monohydrochloride*, N_2H_4,HCl, which forms long needles melting at 89°.

Hydrazine Dihydrobromide, $N_2H_4,2HBr$, and *Hydrazine Hydrobromide*, N_2H_4,HBr, are very similar to the hydrochlorides, and melt at 195° and 80° respectively.

Hydrazine Dihydriodide, $N_2H_4,2HI$, can only be obtained by the action of fuming hydriodic acid on benzalazine, $C_6H_5.CH:N.N:CH.C_6H_5$, and is a very hygroscopic substance which melts at 220°, and becomes brown in the light. The *monohydriodide*, N_2H_4,HI, is formed by the action of iodine on an alkaline solution of hydrazine hydrate:

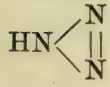
$$5N_2H_4,H_2O + 2I_2 = 4N_2H_4,HI + 5H_2O + N_2.$$

It forms long colourless prisms, melts at 127°, and explodes violently at a higher temperature.

Trihydrazine Dihydriodide, $3N_2H_4,2HI$.—This salt is prepared by the addition of iodine to a solution of hydrazine hydrate in a little alcohol till crystals separate in quantity. It crystallises in large white needles melting at 90°.

Hydrazine Sulphate, N_2H_4,H_2SO_4.—The method of preparation of this salt has been already mentioned in describing the preparation of hydrazine (vol. i. p. 470). It crystallises in thick lustrous tablets or long thin prisms, belonging to the

rhombic system, and is sparingly soluble in cold but readily soluble in hot water, and insoluble in alcohol. It melts at 254° and simultaneously undergoes decomposition, yielding hydrazine sulphite, sulphur dioxide, sulphuretted hydrogen, and sulphur.

Hydrazine Nitride or *Hydrazine Azoimide*, N_5H_5 or N_2H_4.  is obtained by the action of hydrazine hydrate on ammonium azoimide, or azoimide itself, and forms large vitreous prisms, melting at 50°, which deliquesce in the air, and gradually volatilise. It is sparingly soluble in alcohol, from which it crystallises in lustrous plates, and explodes with great violence when quickly heated or touched with a white-hot wire.[1]

[1] Curtius, *Ber.* 1891, **24**, 3348.

THE COPPER GROUP

Copper Cu, Silver Ag. Gold Au

150 THE metals of this sub-group, as has already been pointed out (p. 153), differ very considerably from the other metals of the same group. Like the alkali metals, they form a series of characteristic salts in which the metal is monovalent, but, except in the case of silver, other series of salts are known which are more stable than the first-named series. As is frequently the case with metals having very high atomic weights, gold differs in many respects from the elements of the same sub-group having a lower atomic weight, and also shows considerable resemblance with the elements having nearly the same atomic weight; thus gold resembles platinum and iridium in many respects, and is frequently classed with these metals.

COPPER. Cu = 63·13.

Copper of all the metals is the one which was first employed by man. This is explained by the fact that copper occurs in the native condition, and thus requires no metallurgical treatment. In the Hebrew Scriptures copper is termed *Nehósheth*, a word derived from the root *nahásh*, to glisten. This is translated by Χαλκός in the Septuagint, and this again by *aes* in the Vulgate. By both of the latter words the ancients understood, not only copper, but brass and bronze. Copper was afterwards specially designated as *aes cyprium*, or simply *cyprium*, a name which afterwards became *cuprum*.

The Latin Geber appears to have noticed that copper is easily attacked by acid liquids, and hence it was termed *meretrix metallorum* by the alchemists. Inasmuch as it was derived

from Cyprus, copper was considered to be the metal specially sacred to Venus, and in the writings of the alchemists it is generally known by the name of this goddess and symbolised by ♀. In the works attributed to Basil Valentine we find the first note of the power possessed by iron to precipitate metallic copper from solutions of its salts. In his *Last Testament* we read: "The cement or *ley* from Schmölnitz in Hungary eats iron into slime, and when the iron mud is taken out of the trough it is found to be good ♀ (copper)." In his *Currus Triumphalis Antimonii* he says, "From iron a ♀ (copper) can be got by natural means, as, for instance, by an acrid ley from Hungary which gives to it (the iron) such a metallic colour that it is converted into the best copper."

It would thus appear that this change was regarded as a transmutation of iron into copper, and Paracelsus and many other chemists seem to have held similar views with respect to this reaction. Wedel in 1664 made special inquiry into the nature of the wonderful transmutation of iron into copper by means of this Hungarian liquor; and so late as 1690 Stisser, who was professor of chemistry in Helmstedt, believed that the formation of copper precipitate was a proof of the possibility of the transmutation of metals.

It was long before these erroneous views concerning this precipitation of copper were corrected, although Van Helmont rightly surmised that the copper exists in the solution from which it is precipitated by the iron. Boyle first proved this to be the case, and in his *History of Fluidity and Firmness*,[1] published in the year 1661, he describes the precipitation of copper from its solutions by metallic zinc, and in 1675 in his *Treatise on the Mechanical Causes of Chemical Precipitation*,[2] explains the action of iron upon copper solutions by the supposition that the solvent permits the metal to be precipitated in order to take up the precipitant.

Copper occurs in the native state in various parts of the world, especially, sometimes in enormous masses, in the copper region of Lake Superior, where it occurs in veins traversing red sandstone and trap. It is also found in the same condition in Cornwall, the Faroe Islands, Siberia, and the Urals, and in many localities in North and South America. Native copper almost invariably contains small quantities of silver and a few other metals, such as bismuth, lead, &c. Cupric

[1] *Op.* **1**, p. 377. [2] *Op.* **4**, p. 329.

oxide, CuO, black oxide of copper, also occurs in nature, as tenorite or melaconite, and cuprous oxide, Cu_2O, as cuprite or red copper ore, occurs in larger quantities. Many other copper salts occur native; of these the most important are malachite, $CuCO_3 + Cu(OH)_2$; azurite or blue carbonate of copper, $2\,CuCO_3 + Cu(OH)_2$. Copper also occurs widely distributed in combination with sulphur as vitreous copper, chalcocite, or copper glance, Cu_2S; covellite or indigo copper, CuS; copper pyrites, or chalcopyrite, $CuFeS_2$, and erubescite or purple copper ore, Cu_3FeS_3.

151 *Copper-smelting.*—The methods in use for the extraction of copper differ considerably, according to the nature of the ore from which the metal is to be derived. Both dry and wet processes of extraction are employed, the greater quantity of the metal being obtained by the former plan.

Two different classes of dry processes are successfully at work, namely (1) roasting in reverberatory furnaces, and (2) reduction in blast furnaces. The first method, frequently known as the *Welsh* or *English process*, is chiefly carried out in the Swansea district of South Wales, and is adapted to all kinds of copper ore, and the greater portion of the metal brought into the market is smelted by this method.

In carrying out the process a mixture of copper ores is usually employed, consisting of copper pyrites and copper carbonates mixed with iron pyrites containing silicates and gangue, mostly consisting of quartz. In obtaining the pure metal six distinct processes are required, viz.:

(1) Calcining the mixed ore.
(2) Preparing "coarse metal."
(3) Calcining the "coarse metal."
(4) Preparing "fine metal."
(5) Roasting to obtain metallic copper.
(6) Refining.

The calcination of the crude ores is carried out by roasting in heaps, stalls, kilns, or reverberatory furnaces. The first-named method is the simplest, the ore being broken into a suitable size, mixed with fuel, and arranged in such a manner as to allow of the admission of the requisite quantity of air, and the fuel then ignited. Stalls consist of heaps, which are enclosed on three sides by walls, and are built up in a similar manner to the

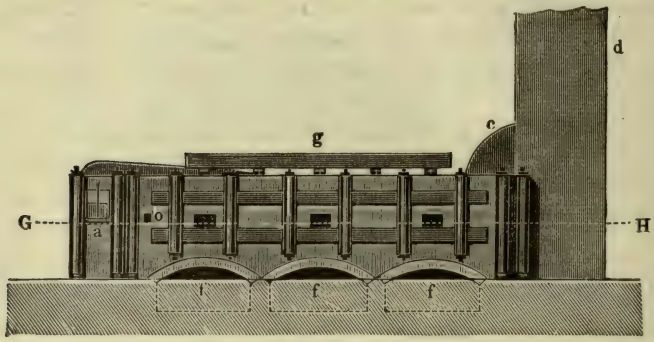


FIG. 63.

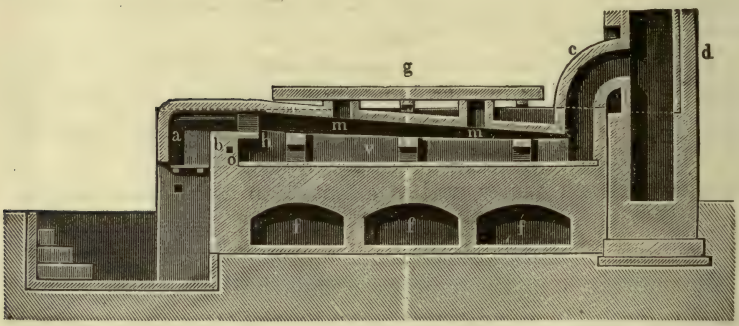


FIG. 64.

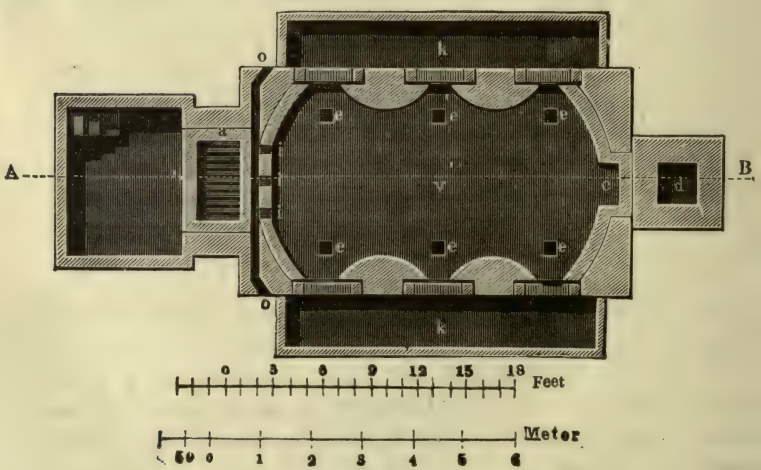


FIG. 65.

former. In both cases the whole of the sulphur dioxide evolved is usually lost and passes away into the atmosphere.

Figs. 63, 64, and 65 show the construction of the ordinary *calcining furnace*. In some copper-works the furnaces are heated with gas, Figs. 66 and 67, and Siemens' regenerative apparatus has been successfully applied. The mixture of ore is brought on to the bed of the furnace from the cast-iron trough, the bottom of which is provided with two sliding-doors. From three to three-and-a-half tons of ore is introduced by withdrawing these doors, and then spread evenly over the floor of the furnace by long iron rakes introduced through the working-doors, of which there are three on each side. The ore is stirred occasionally with iron paddles to expose a fresh surface to the oxidising action of the hot air, until after the lapse of from twelve to twenty-four hours sufficient quantities of the oxides of copper and iron have been formed. The roasted ore is then raked through the openings (*e e*, Fig. 65), which had hitherto been covered by slabs of fire brick, into the arched chambers (*f f*, Fig. 64), where it is allowed to cool.

Ores poor in sulphur are usually roasted in kilns, one of the forms most frequently used being the Gerstenhofer calciner; this consists of a rectangular kiln about 20 feet high, in which triangular fire bars of iron or fireclay are fixed horizontally in rows at distances of about one foot. When the kiln has been heated, the ore in a finely powdered state is passed by means of feed rollers into the top of the furnace and works its way down through the fire bars, meeting a current of air coming in the opposite direction by which it is oxidised, the heat given off by the oxidation maintaining the necessary temperature. The oxidised ore is removed from the bottom of the kiln, whilst the sulphur dioxide passes away with the excess of air from the top. Ores rich in sulphur cannot be treated in this kiln, as they cake together on the bars and prevent the passage of the air.

In addition to these, revolving cylinders are now sometimes employed; these are similar in principle to the Oxland calciner employed in roasting tin ores. (See Tin.)

In all cases the result of the process is the same, viz. the partial oxidation of the sulphides of copper and iron, with formation of the corresponding oxides, and the conversion of copper carbonate into oxide.

In the second process the roasted ore is mixed with "metal

slag" derived from the "fine metal" process, and strongly heated in a reverberatory furnace, the object being to obtain a fused mass or *regulus* consisting of a mixture of the sulphides of

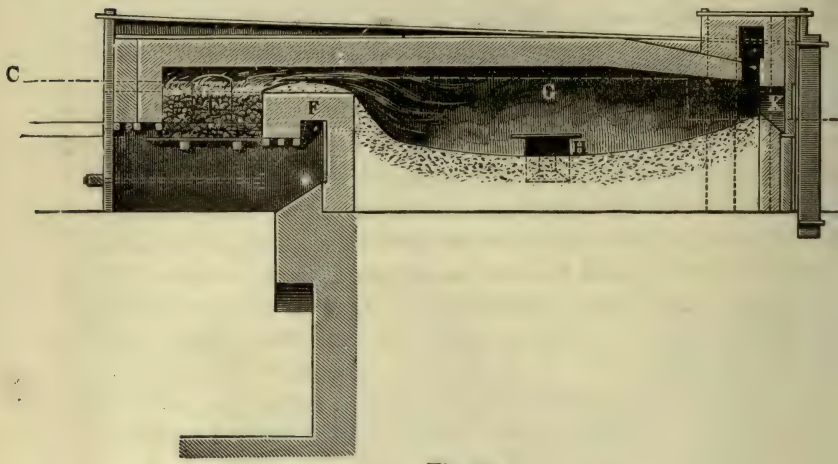


Fig. 66.

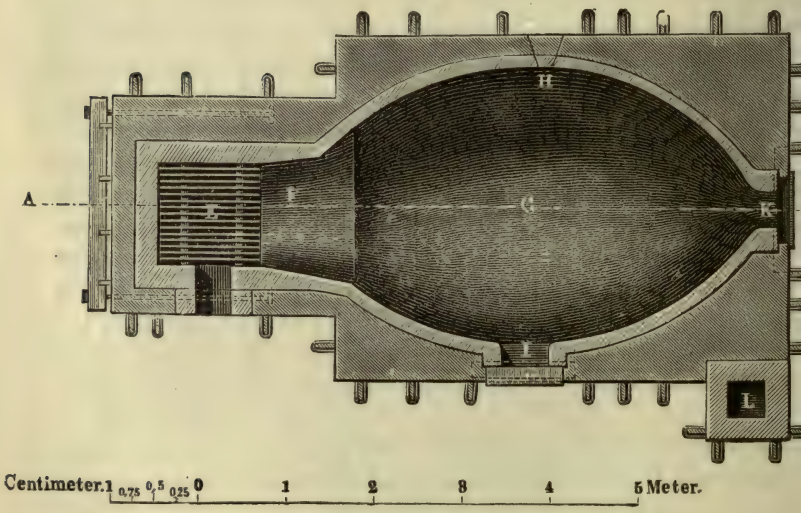


Fig. 67.

copper and iron, termed *coarse metal*, whilst a slag is at the same time formed which consists of a silicate of iron and contains little or no copper, and is called *ore-furnace slag*. The tempera-

ture needed in this melting process is much higher than that required in the previous operation, and the chief chemical changes which go on are simple enough. The copper oxide of the roasted ore undergoes decomposition with a portion of the sulphide of iron with formation of copper sulphide and oxide of iron; this latter oxide then combining with the silica present to form a fusible slag of iron silicate. In order to obtain by this means an ore-furnace slag free from copper, it is found that the mixture of ore brought into the furnace must not contain more than 14 per cent. of copper, whilst, on the other hand, the percentage of copper ought not to sink below 9, otherwise the consumption of fuel becomes extravagant. The coarse metal, or crude copper sulphide, usually contains about 35 per cent. of copper and about 23 per cent. of sulphur. The fused coarse metal is usually run off, after skimming, through the tap-hole into water, and thus obtained in a granulated condition.

The third operation is to calcine the granulated or crushed regulus, or coarse metal, for the purpose of oxidising that portion of the sulphur which is combined with iron, so that when again melted, in the fourth operation, with the addition of *roaster-slag*, *refinery slag*, and a certain proportion of oxidised ores such as the carbonate or oxide, a nearly pure copper sul phide, Cu_2S, called *white-metal* or *fine-metal* and containing about 75 per cent. of copper, is obtained.

If the amount of oxidised ore be insufficient, the product contains sulphide of iron and is then known from its colour as "blue metal," whilst if an excess be employed some of the copper sulphide is reduced, and sulphur dioxide evolved; the latter in its attempt to escape gives the surface a pimply appearance, the product being therefore known as "pimple-metal."

The melting furnace used in this last operation is identical in construction with that employed in the first fusion, and the slags which are formed chiefly consist of iron silicate, but contain some quantity of copper, and are termed *metal-slags;* these are employed, as has been stated, in the first melting process.

The white-metal is then subjected to a roasting process carried on in a reverberatory furnace in which air-holes are left. In this way a portion of the oxide formed decomposes a part of the sulphide, with production of metallic copper and sulphur dioxide:—

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

The metal thus reduced is filled with cavities, and hence it is termed *blister-copper*. It still contains from 2 to 3 per cent. of impurities, chiefly consisting of iron and other metals. In cases where a very impure ore has to be dealt with, it has been found of great advantage to replace the ordinary silica lining of the roaster furnaces and also of the refinery furnaces employed in the subsequent process by a basic lining, a purer product and much less slag being obtained, arsenic especially being more readily eliminated.[1]

To remove the above 2 to 3 per cent. of impurities, the blister-copper is subjected to the sixth and last, or refining process. For this purpose the blister-copper is again fused in a melting-furnace constructed like the others, except that its floor is inclined towards a point near the door and near the chimney. Upon this floor a charge of about eight tons of blister-copper is brought, and the slags having been removed by skimming from the surface of the molten metal, this is well stirred up, or *rabbled*. The metal in this condition is termed *dry copper*. In this state it is however unfit for use, as it contains a small proportion of oxygen, in combination as cuprous oxide, which renders it brittle. To eliminate this, the metal has to be *toughened*. This is effected by covering the surface of the molten metal by a thin layer of anthracite, which reduces the oxide contained in the surface layer of metal, whilst that contained in the lower portions is removed by plunging a young pole of green birch-wood into the molten metal. Large volumes of reducing gases, consisting of hydrocarbons and carbon monoxide, are thus evolved, and the metal boils up violently, the oxide being effectually reduced. After the *poled* metal has remained quiescent for a few minutes a sample is removed by the refiner, cast into a mould, and the casting first half cut through with a cold chisel, and then bent backwards and forwards until the piece breaks off. From the appearance and colour of the fractured surface an experienced eye can at once decide whether the copper has arrived at what is termed the *tough-pitch*. When this is reached, the charge must be withdrawn from the furnace as rapidly as possible and cast into iron moulds, in order to prevent a second oxidation occurring. Sometimes the molten metal becomes what is called *over-poled*, and if this be the case the metal must be exposed to the air for a short time to bring it back again to the tough-pitch.

Figs. 68 and 69 show the construction of a melting-furnace

[1] Gilchrist, *Journ. Soc. Chem. Ind.* 1891, 4.

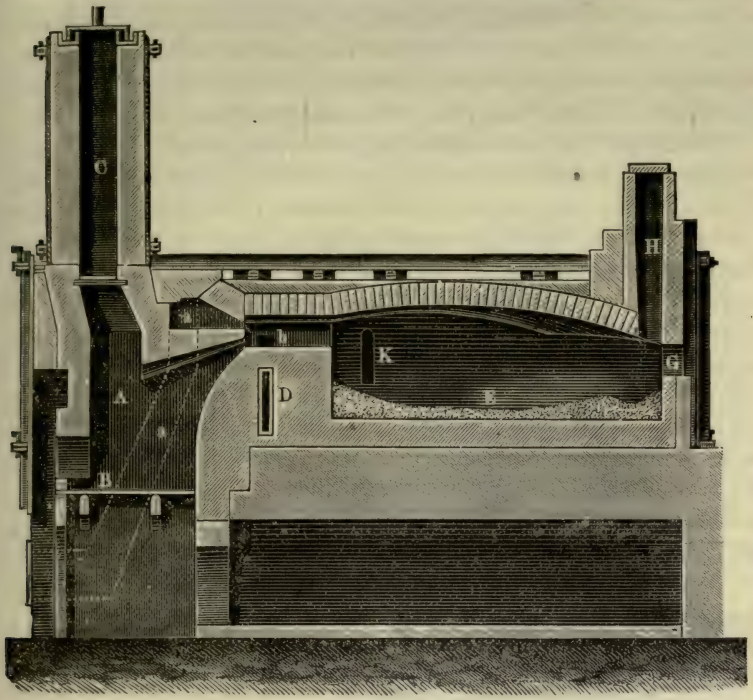


FIG. 68.

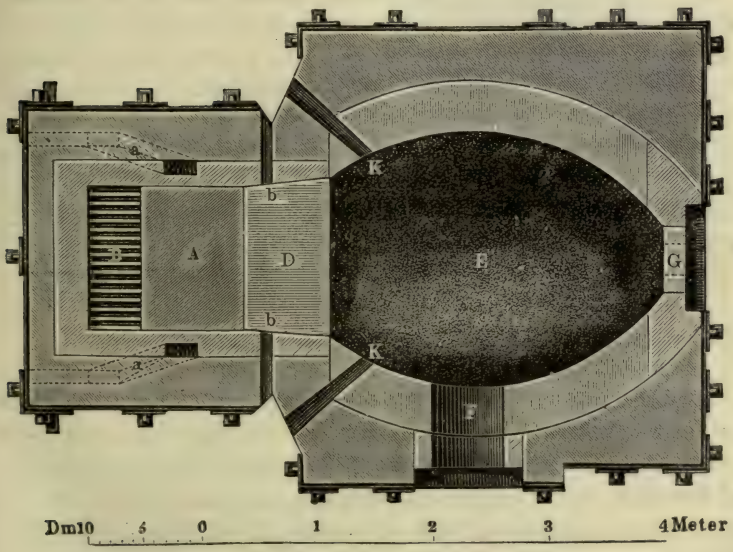


FIG. 69.

with a gas-generator (A) fired with coal which is filled from the shaft (C). The air necessary for the combustion of the generated gas is admitted by the opening (*b b*), whilst that required for the oxidation of the charge enters by the openings (K K).

The subject of the toughening of copper and of the removal of the non-metallic impurities contained in commercial copper, is somewhat complex, and has received much attention from metallurgists. From the experiments of Abel[1] it appears that toughened copper always contains a certain amount of oxygen present as suboxide, and this agrees with the observation of copper-smelters, who find that the whole batch may become over-poled in a few seconds, this being explained by the fact that the whole of the oxygen has been withdrawn. According to Hampe,[2] on the other hand, the phenomenon of the over-poling copper depends partly on the absorption of carbon monoxide and hydrocarbons, and especially on the reduction of small quantities of lead oxide and bismuth oxide, which the copper contains, so that if these bodies be not present no over-poling occurs.

When copper is intended for rolling, it has long been the practice to add a little lead to the tough-pitch metal, and for certain purposes, such as the construction of locomotive fire-boxes, the presence of small quantities of phosphorus has been found of great advantage.

Almost all copper ores contain a certain quantity of arsenic, which is mostly evolved as arsenious oxide together with the sulphur dioxide in the roasting process; in many works this is recovered by passing through long flues, where it is deposited, the sulphur dioxide being then employed for the production of sulphuric acid. In many cases the dilution of the sulphur dioxide by the air renders this impossible, but it is nevertheless feasible by the adoption of suitable measures to prevent much of the damage and nuisance caused by the "copper smoke."

Reduction of Copper Ores in Blast Furnaces.

152 *The Mansfeld process of Copper-smelting.*—The well-known cuprous schist or "kupferschiefer" of the Germans, has been worked for copper for a long time. Agricola, writing in the middle of the sixteenth century, describes the methods adopted in his time near Mansfeld for the extraction of the metal. The first

[1] *Journ. Chem. Soc.* 1864, 172. [2] *Chem. Centr.* 1875, 378.

operation consists in the roasting or burning of the schist in heaps. In this process the bituminous matter is burnt off, the water and arsenic expelled, and a portion of the sulphur removed. In process No. 2, the roasted ore is mixed with about from 5 to 8 per cent. of slag from the "black copper" process and fluor-

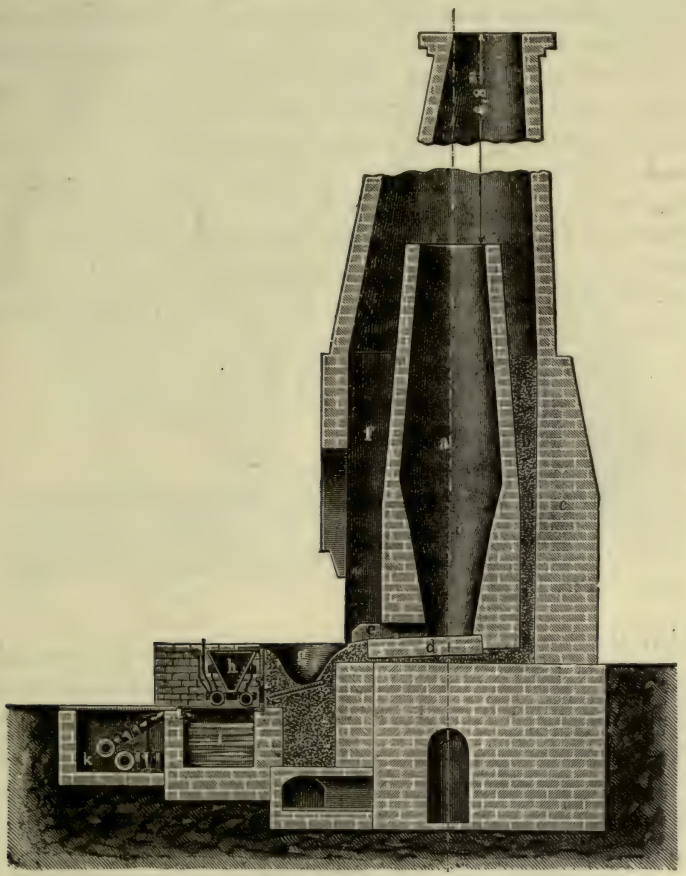


Fig. 70.

spar, the yield being coarse metal and slag containing very little copper. This operation is conducted in a blast-furnace or cupola from sixteen to thirty feet in height, supplied by air from two tuyeres, and the coarse metal, as it forms, runs out of the furnace into basins placed to receive it. The coarse metal, or "rohstein," containing from 20 to 60 per cent. of copper according

to the nature of the ore, is next roasted, and the calcined ore melted for fine metal, or "spurstein."

The Mansfeld ores contain silver, usually about 0·5 to 100 of copper, and this is well worth extraction. In order to effect this, the fine metal is ground between mill-stones, and the powder carefully roasted. In this process the copper is mainly converted into an insoluble oxide, whilst the silver is all transformed into the soluble sulphate, and can be completely extracted by lixiviation (Ziervogel's process). The insoluble copper oxide and sulphide termed "gaarrost" is then fused with slag in a blast-furnace, closely resembling that shown in Fig. 70, and a rich regulus of black copper is obtained; it contains about 98 per cent. of copper, the remainder consisting of iron together with small quantities of silver and antimony, the colour being due to a thin coating of cupric oxide. The black copper is lastly refined in a small furnace termed a refining hearth (Figs. 71 and 72), in

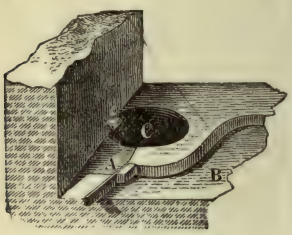


Fig. 71.

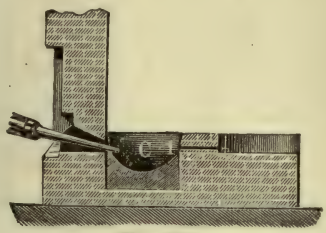


Fig. 72.

which the impure metal is melted in contact with charcoal, a blast of air being supplied by the tuyeres, and samples of the metal withdrawn from time to time to ascertain when the process is complete. The copper thus obtained is, however, not of the highest quality, and it must be subjected to a process of toughening in order to enable it to attain its maximum degree of malleability.

During recent years great advances have been made in the reduction of copper ores by blast-furnaces, especially in America. The greatest improvement consists in the replacement of the brick blast-furnaces by water-jacketed iron furnaces. One of the best forms of furnace is that of Herreshoff, a sectional elevation of which is shown in Fig. 73, and a sectional plan in Fig. 74. The main furnace, A, has an elliptical section, and consists of a double casing of iron, A, B, C, through which water is continually circulated; the bottom of the

furnace, E, is lined with fire-brick or fire-clay. The roasted ore, mixed with coke or anthracite, and the slag from a later

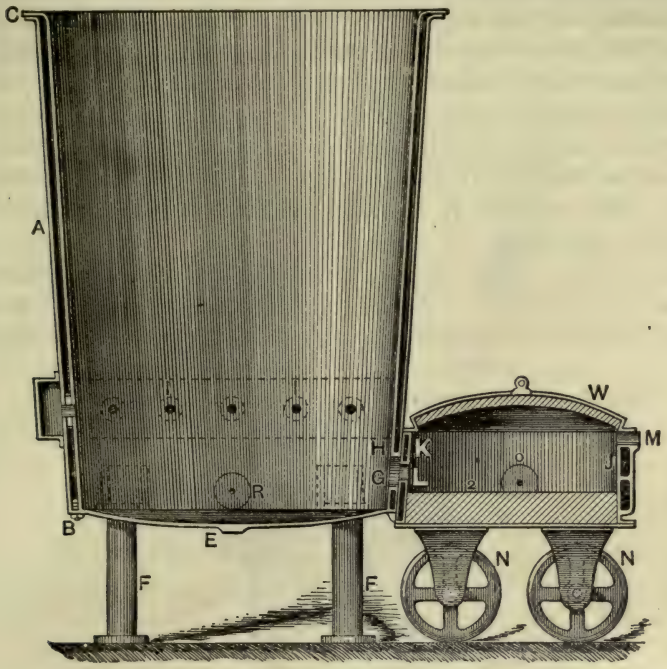


FIG. 73.

process, which consists chiefly of iron silicate with a little copper, is introduced at the top of the furnace, the air being

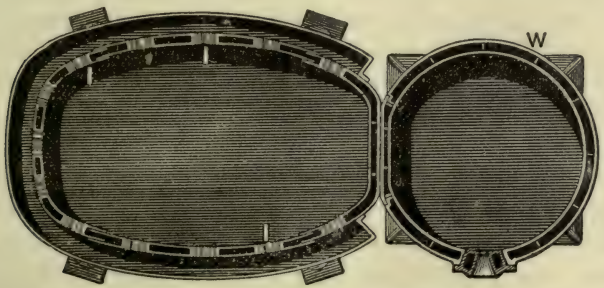


FIG. 74.

forced through the tuyeres I I. The products, which consist of "matte" (corresponding to the "coarse metal" of the Welsh

process) and slag, accumulate in the bottom of the furnace and then overflow continuously into the "fore-hearth" W, the end elevation of which is shown in Fig. 75; this is frequently mounted on wheels, N N, for convenience of moving. The slag then flows away almost continuously from the opening M, the matte being run off by the tap-hole, O, as occasion requires. This is then calcined and usually treated in reverberatory furnaces as in the Welsh method, although in many works in America the blast-furnace is employed for the later processes also. The refining is invariably carried out in the manner already described.

Application of the Bessemer process to Copper-smelting.—Mention must also be made of the reduction of metallic copper in the Bessemer converter by the Manhès process, although at

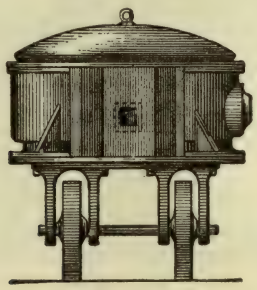


Fig. 75.

present this has not been extensively adopted. The principle involved is the same as that of the Bessemer iron process, viz., the removal of the foreign substances by the passage of air through the molten mass. In the production of copper from coarse metal, the action must be carried out in two different operations. In the first, air is blown through the molten mass until the "metal" contains about 75 per cent. of copper, the sulphur and iron being oxidised and the latter combining with the silica of the furnace lining to form a slag of iron silicate; when the "metal" contains the above amount of copper the contents are emptied, the slag removed and the fine metal subjected to the same treatment in a second converter and thus reduced to metallic copper. The chief difficulty encountered in the process is due to the fact that the heat produced by the oxidation of the sulphur is small, and that, therefore, as

the reduction proceeds, the tuyeres frequently become blocked by solidified metal. This has been largely overcome by placing the tuyeres at the sides of the furnace, some distance above the bottom, and so arranging them that their direction can be altered during the blow, thus making it unnecessary to force the air through the reduced copper, which sinks to the bottom.

153 *Wet Copper Extraction Processes.*—Upwards of half a million tons of iron pyrites, containing on an average 3 per cent. of copper, are annually burnt in the sulphuric acid works of this country. The residual oxide of iron, known as burnt pyrites, or *blue billy*, is too poor in copper to render it possible to apply to it any of the ordinary dry-smelting operations. Processes for accomplishing this end have been proposed by Longmaid and Henderson, and are now carried out on a large scale, and known as the wet copper extraction processes. These operations depend upon the fact that if the ground-burnt ore be mixed with from 12 to 15 per cent. of coarsely crushed rock-salt, and the mixture properly calcined, the whole of the copper is converted into a soluble cupric chloride. The roasted mass is then lixiviated, and the copper contained in solution thrown down as metal by scrap-iron, any silver contained in the solution being previously precipitated as silver iodide by the addition of potassium iodide. The calcination is usually carried on in long furnaces shown in Figs. 76, 77, 78, and 79, the mixture of ore and salt being introduced through hoppers placed above the furnace; the temperature is kept at a dull red-heat and the mass frequently stirred. The ordinary furnace charge is 3 tons 5 cwts., and the operation lasts about six hours. It is found that the success of the working of the process depends upon the relative amounts of sulphur and copper existing in the ore, the sulphur exceeding the copper by about 0·5 per cent. If the proportion of sulphur in the burnt ore be less than this, a sufficient quantity of raw pyrites must be added. During the calcination considerable quantities of chlorine and hydrochloric acid gases are evolved, together with some vapours of ferric and cupric chlorides. In order to prevent these noxious vapours from passing into the atmosphere, the exit flue from the furnace is connected with a wash-tower filled with open brickwork, down which a current of water passes. The precipitate of metallic copper, thrown down from the liquors by scrap-iron, contains from 70 to 80 per cent. of copper, and it is either smelted directly for blister-copper,

or fused with the fine metal, Cu_2S, of the dry process, then roasted, and afterwards worked up to marketable copper by the process already described.

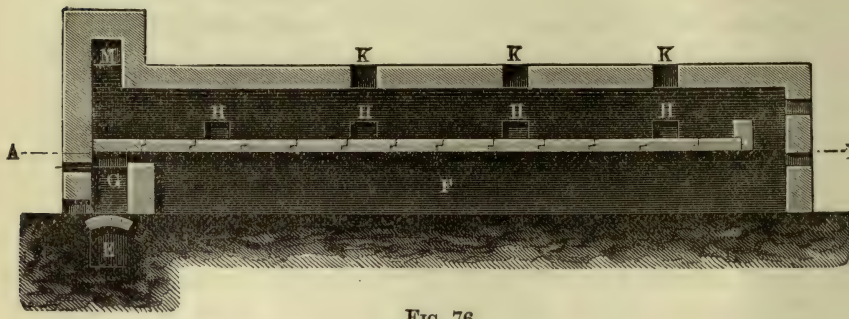


Fig. 76.

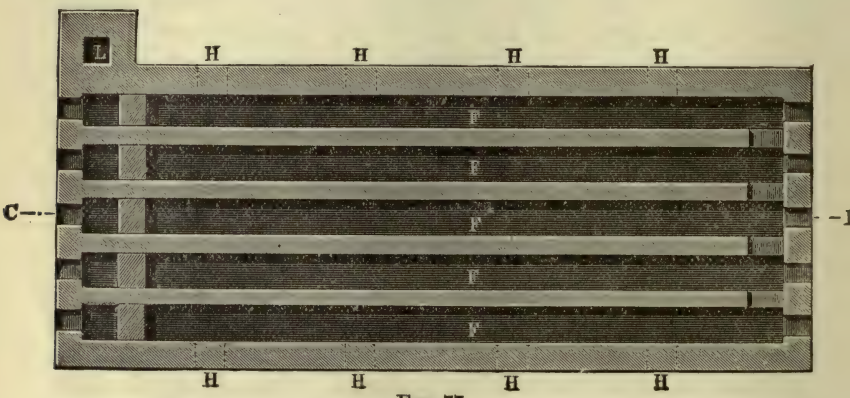


Fig. 77.

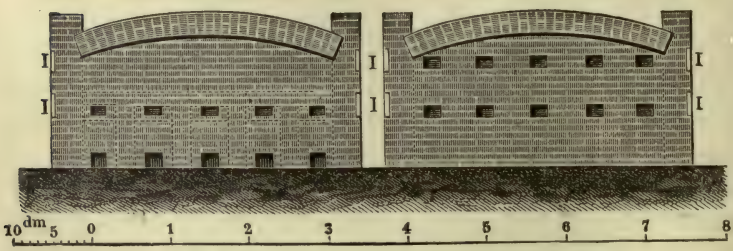


Fig. 78. Fig. 79.

Another extraction process is that of Hunt and Douglas.[1] According to this, the ores containing carbonates or oxides

[1] *Engineering*, **22**, 419.

are simply heated, whilst those containing sulphides must be roasted. The ore is then treated with a solution prepared by dissolving 120 parts of common salt or 112 parts of calcium chloride, and 280 parts of ferrous sulphate in 1,000 parts of water, and then adding 200 parts of common salt. The process depends upon the fact that ferrous chloride, $FeCl_2$, is thus formed, which in contact with common salt converts the copper oxides into chlorides. If cuprous oxide be present, metallic copper is at once precipitated:—

$$3Cu_2O + 2FeCl_2 = 2Cu + 2Cu_2Cl_2 + Fe_2O_3.$$

Cupric oxide is decomposed as follows:—

$$3CuO + 2FeCl_2 = Cu_2Cl_2 + CuCl_2 + Fe_2O_3.$$

Cuprous chloride, although insoluble in water, is held in solution in the presence of the other chlorides, and then decomposed by iron together with the cupric chloride.

Electrolytic Refinement of Copper.

Copper is now refined on the large scale by means of electrolysis, this process being especially applicable in the case of impure copper containing silver or gold. For this purpose the copper is cast into slabs in which whilst still molten a copper hook is inserted to serve as a connection. The slabs are placed in a wooden tank lined with lead, and form the anodes, thin sheets of pure copper being employed as cathodes; the solution in the tank consists of $\frac{1}{2}$ lb. of sulphuric acid and 2 lbs. of crystallised copper sulphate per gallon. When an electric current is passed through the solution, the impurities, with the exception of silver and gold, dissolve before the copper, and with suitable working the latter is deposited on the cathodes before any of the metals which first passed into solution. The silver, being almost insoluble in the dilute sulphuric acid used, falls to the bottom of the bath together with the gold, forming a mud which is removed and worked up for the two metals. To obtain a pure copper careful attention to detail is required, but with due care a metal containing 99·8 per cent. of copper may be obtained.

Electrotyping Process.

154 The electrolytic method for the decomposition of copper is employed not only for the refining of metallic copper, but also very largely for obtaining a coating of metallic copper on any suitable object, the latter being employed as the cathode in a bath of copper sulphate solution, the anode consisting of slabs of metallic copper. This industry dates back much further than that of the electrolytic refinement of copper; the latter being in reality an offspring of the electrotyping process.

In the year 1836 De la Rue, when using a Daniell's battery, observed "that the copper plate is covered with a coating of metallic copper which is continually being deposited; and so perfect is the sheet of copper thus formed, that on being stripped off it has the counterpart of every scratch of the plate on which it is deposited."[1] This observation was followed up by other physicists, and in 1839 Professor Jacobi of St. Petersburg published his galvano-plastic process, "a method of converting any line however fine, engraved on copper, into a relief by galvanic process, applicable to copper-plate engravings, medals, stereotype plates, ornaments, and to making calico-printing blocks and patterns for paper-hanging."[2] In the same year T. Spencer of Liverpool read a paper on the "Electrotype Process," to the Liverpool Polytechnic Society, and also in 1839 J. C. Jordan published results of experiments made with the same object.[3]

Electrotyping in copper has become a most important branch of industry, statues and other works of art being in this way largely reproduced. Several of these made by this process in the celebrated works of Messrs. Elkington of Birmingham, and Messrs. Christophle of Paris, have attained colossal proportions.

For the purpose of reproducing statues, busts, and similar objects, casts of the original in gypsum or models in gutta-percha are saturated with oil, coated with graphite to give the surface the necessary conducting power, guiding wires connected to various parts of the surface, and the object then made the cathode in a bath of copper sulphate solution. When the

[1] *Phil. Mag.* [3], 484. [2] *Athenæum*, May 4, 1839.

[3] For a detailed account of these discoveries, see Gore's *Art of Electro-Metallurgy.*

coating is $\frac{1}{16}$th of an inch thick the process is stopped, the copper cut through in several places and the plaster core extracted. The inner surface of the various parts is then subjected to the action of sulphuretted hydrogen to coat it with a thin layer of sulphide, and these again placed in the copper sulphate bath as the anode. As soon as the deposit on the interior is of sufficient thickness the parts are removed, the thin outer shell of copper torn off and the parts then joined together.

The method for the reproduction of fragile articles such as fruit, flowers, insects, in copper may here be mentioned. These are first coated with silver by means of a saturated solution of silver nitrate in hot alcohol; they are dipped for a moment into this solution, the alcohol allowed to evaporate and the film of the salt left upon the object reduced to metal by bringing it into the vapour emitted by a solution of phosphorus in carbon bisulphide. The articles are then coated in a solution of copper sulphate by the method already described.

For the purpose of covering iron, an alkaline solution of copper cyanide in potassium cyanide is employed. On dipping the iron or steel article into this solution a thin deposit of copper is obtained and upon this a coating of silver or gold can easily be deposited. For the purpose of obtaining a thicker deposit of copper on iron, the operation is conducted as described and the object then placed in a copper sulphate depositing bath. The solution, according to Wilde's process, is maintained in a constant state of rotation, and the iron heated to 90° before it is placed in the warm solution of cyanide, no hydrogen then being liberated on the copper, so that the latter adheres more closely to the iron. The process is now successfully applied to the economical production of coppered cast-iron rollers for calico-printing. When a new pattern is required on the roller one-half of the copper is turned off and restored to its original thickness by electro-deposition at a small cost. The maintenance of the rollers to a standard size is a great advantage.

An important branch of electrotyping is that by which wood-cuts can be copied and their number thus indefinitely increased. This is accomplished by obtaining a reverse of the wood-cut in gutta-percha softened in hot water; the cast thus obtained is then covered with finely divided graphite powder, placed as the negative pole of a battery and allowed to remain in the copper solution until the metal is deposited in a film of suffi-

cient thickness. It is then taken out, and, to give it the requisite solidity, the back of it is filled with molten type-metal or with fusible solder. In the same way engravings from either steel or copper plates may be copied, and the same process can be applied to type-metal, the galvano-plastic being used in some cases in preference to the stereotype-process.

Properties of Copper.—Commercial copper usually contains traces of the other metals which are present in the ores, and in addition to these not infrequently arsenic, sulphur, and oxygen. Pure metallic copper is obtained either by heating the pure oxide in hydrogen, or by the electrolysis of a solution of pure copper sulphate by means of platinum electrodes.

Copper possesses a peculiar red colour and bright metallic lustre. The true copper-red colour is, however, not seen by a single reflection, and is only observed when the light entering the eye has been many times reflected from the surface of the copper. This is well seen if a piece of straight copper foil be bent at an acute angle and held before the observer; the fine deep red copper colour is noticed near the point at which the two copper surfaces approach.

Copper is found crystallised in the native state in regular octohedra; crystals of the same form are also found as an artificial refinery product. If a piece of phosphorus be allowed to remain for some months in contact with a clean copper wire under a solution of copper sulphate, single octohedra of metallic copper are formed together with copper phosphide (Wöhler), and a similar artificial formation of crystallised copper is observed in Golding-Bird's decomposing cell,[1] as well as in the cells of Meidinger's battery. In both these cases the metal is deposited from solution very slowly.

Copper is one of the toughest of metals. It is very malleable, and may be hammered or rolled into thin leaf (Dutch metal), or drawn into fine wire. After hammering it possesses a finely fibrous or silky fracture. Very slight admixture of other metals makes it more brittle, and imparts to it a less distinctly fibrous nature. Native copper has a specific gravity of 8·94; cast copper, probably because it always contains small cavities, has a specific gravity of 8·92; rolled or hammered copper 8·95; and pure electrolytic copper 8·945 (Hampe). Very thin copper leaf transmits a greenish-blue light. When a solution of copper sulphate is allowed to remain in contact with pure zinc,

[1] *Phil. Trans.* 1837, 37.

pure metallic copper is deposited as a fine spongy mass, which after washing and drying forms a soft impalpable dark-red powder.

Copper melts at 1080°·5;[1] in the molten state it possesses a greenish-blue colour. When heated at a temperature just below that of its melting-point copper becomes so brittle that it can be pounded in a mortar. On passing from the liquid to the solid state copper expands. Molten copper possesses the power of absorbing different gases, which are evolved in the form of bubbles when the metal cools, or give rise to the peculiar phenomenon known as "spitting," when a solid crust has already been formed on the surface. Spongy copper absorbs at a red-heat 0·6 times its volume of hydrogen, whilst copper wire absorbs 0·308 times its volume (Graham). Copper may be readily volatilised in an electrical furnace and condenses in globules, the vapour forming cupric oxide in contact with air.

Metallic copper is largely used for a great variety of technical and domestic purposes, being especially valuable from its toughness. Next to silver, copper is the best conductor of electricity, and hence pure copper is very largely employed for electric light mains and submarine telegraphs. The purest copper must be employed, as very small quantities of impurities lower the conductivity to a very large extent.

Alloys of Copper.—Copper unites with a number of other metals to form alloys, many of which are of great technical importance. Among these may be mentioned brass, an alloy of copper and zinc, bronze, gun-metal, and bell metal, which are alloys of copper and tin, and German silver which is an alloy of copper and nickel. A description of these will be found under the metal forming the second constituent of the alloy.

[1] Heycock and Neville, *Journ. Chem. Soc.* 1895, i. 190.

COPPER AND OXYGEN.

155 These elements form five compounds as follows:—

Copper quadrantoxide, Cu_4O.
Copper trientoxide Cu_3O.
Cuprous oxide, Cu_2O.
Cupric oxide, CuO.
Copper dioxide or cupric peroxide, CuO_2.

Of these oxides the third and fourth have long been known, as they are formed when metallic copper is heated in the air. Copper scale, which falls from hot metallic copper when it is worked with the hammer, is a mixture of these two oxides. The portion of the scale next to the metal consists of the red cuprous oxide while the outside portion is composed of black cupric oxide. Dioscorides and Pliny mention the existence of the red compound, indeed they distinguished two varieties, the one obtained in the form of a finely divided powder by pouring water on to the surface of a freshly melted copper and termed *flos aeris*, and the other obtained as copper scale and termed *aeris squama*. Geber explained the calcination of copper by the combustion of the sulphur which this metal was supposed to contain (vol. i. p. 5), and many later chemists speak of copper as being more or less calxed. It was not, however, until the year 1798 that Proust distinctly stated that the black and red calces of copper were two distinct oxidation products.

They have the composition Cu_2O and CuO respectively, and give rise to characteristic series of salts, known as the *cuprous* and *cupric* salts. In addition, lower oxides of the formulæ, Cu_4O and Cu_3O and a peroxide CuO_2 have been prepared, none of which yield salts. Hydrated mixed oxides of the formulæ $Cu_3O_2+2H_2O$ and $Cu_4O_3+5H_2O$ have also been described by Siewert.[1]

156 *Cuprous Oxide*, Cu_2O.—This oxide occurs as cuprite or red copper ore, crystallising in octohedra and in other simple or complex forms of the regular system, having a specific gravity of 5·75. It possesses a bright red or brownish red colour, frequently exhibiting a diamond lustre; it also occurs in the

[1] *Zeitschr. Chem.* 1866, 363.

massive state. In the mineral chalcotrichite it forms a hair-like mass consisting of small cubical crystals elongated in the direction of one of the axes.

Cuprous oxide may be artificially obtained by heating thick copper wire in a muffle for half an hour at a white heat, and then for some hours to dull redness; small dark crystals of the oxide then cover the surface of the metallic bead. It is also obtained by heating cupric oxide in a similar manner, but if too strongly heated the cuprous oxide loses a further quantity of oxygen. The finely divided copper obtained by reducing a copper salt in hydrogen at as low a temperature as possible combines with atmospheric oxygen on exposure to the air with formation of cuprous oxide. It may be obtained in the wet way by reducing an alkaline copper solution with sugar, the oxide being deposited on warming as a bright red crystalline powder.

Cuprous oxide is also formed by the slow oxidation of the metal under water. Sage, in the year 1773, pointed out that the remains of a statue which had long lain under water were partially converted into this oxide, and J. Davy observed that an antique helmet found in the sea near Corfu, was covered with crystals of metallic copper as well as of cuprous oxide. It has also been obtained in the crystalline state by the slow galvanic decomposition of copper sulphate.[1]

Commercial cuprous oxide has a specific gravity of from 5·34 to 5·37, and the more finely it is divided the finer red does its colour become. It fuses at a red-heat and colours glass red. This latter property was known to the ancients, and in the middle ages many artificers understood the art of producing the red copper glass. The knowledge of this process was, however, completely lost in later times, and it was not until about the year 1827, that Bontemps in France and Engelhardt in Germany succeeded in reviving the manufacture of this ancient red glass.

Cuprous Hydroxide, $Cu_8O_3(OH)_2 = 4Cu_2O + H_2O$, falls as a bright yellow precipitate when cuprous chloride is decomposed by potash or soda. This precipitate contains only three per cent. of water which cannot be driven off below 360°. The hydroxide easily absorbs oxygen and becomes of a blue colour when exposed to the air. It dissolves in ammonia, as does cuprous oxide itself, forming a colourless liquid, which, on

[1] Golding-Bird, *Phil. Trans.* 1837, 37.

exposure to the air, quickly oxidises and becomes of a dark blue colour.

The oxide and hydroxide correspond to the series of cuprous salts in which copper acts as a monad. These are mostly white salts which are insoluble in water, and readily undergo oxidation with formation of cupric salts.

157 *Cupric Oxide*, CuO.—This substance occurs as tenorite and melaconite as a dark earthy mass or in bright lustrous laminæ and more rarely in cubes. It can be artificially produced by the gentle ignition of the nitrate, carbonate, or hydroxide. Thus obtained it is a black hygroscopic powder which when strongly heated first cakes together and then fuses at about the melting point of copper, and loses oxygen, forming cuprous oxide or Cu_3O according to the temperature. If the amorphous oxide be ignited with five times its weight of caustic potash it becomes crystalline, and regular tetrahedra possessing a metallic lustre are formed (Becquerel). In copper refineries the occurrence of a crystalline oxide has also been observed. When heated in the presence of hydrogen, carbon monoxide, marsh-gas, and other carbon compounds, it is easily reduced to the metallic state with formation of water and carbon dioxide, and hence it is largely used in the ultimate analysis of organic compounds. Cupric oxide when brought in contact with fused glass imparts to it a fine light green colour; this was known to the ancients as well as to the later alchemists who rediscovered the fact, and found that artificial emeralds could be prepared by means of copper. The writer known as Basil Valentine says "the emerald contains sulphur veneris," and the writers of the sixteenth century who treat of the artificial production of gems all mention the fact that copper calx colours glass green.

Cupric Hydroxide, $Cu(OH)_2$, is obtained as a light blue precipitate by decomposing a solution of a cupric salt in the cold with an alkali. This precipitate, however, almost always contains a considerable quantity of alkali, and the hydroxide is obtained in a purer state by adding sal-ammoniac to the solution before precipitation, and then washing the precipitate well with warm water. The compound, after having been dried over lime, does not undergo loss of water on heating to 100°, but if the freshly precipitated oxide be boiled with water it soon becomes black being converted into a hydrate having the composition $Cu_3O_2(OH)_2 = Cu(OH)_2 + 2CuO$. Copper hydroxide dissolves readily in aqueous ammonia yielding a beautiful dark blue

liquid which is also produced when copper is allowed to remain in contact with aqueous ammonia, and the liquid exposed to the air. When largely diluted with water or treated with strong caustic potash, cupric hydroxide separates out from the solution, and on heating this, the black hydrate is precipitated. The solution of copper oxide in ammonia (Schweizer's reagent) possesses the property of dissolving cellulose (cotton-wool, linen, filter-paper, &c.).[1]

The above oxide and hydroxide yield the cupric salts on treatment with acids, the copper acting as a dyad. The salts formed with colourless acids are colourless when anhydrous, but the hydrated salts are blue or green, the aqueous solutions having a similar colour. They combine with ammonia forming peculiar compounds which dissolve in water forming deep blue solutions. The soluble salts have an unpleasant metallic taste and have an acid reaction to litmus.

In large doses the copper salts are poisonous, causing vomiting, but in small doses they have very little action, the cases of poisoning formerly supposed to have taken place from the presence of copper in food, being probably due to the presence of organic decomposition products such as the ptomaïnes.[2]

Copper Quadrantoxide, Cu_4O, is formed by careful addition of a solution of copper sulphate to a well cooled dilute solution of stannous chloride in caustic potash, the cupric hydroxide first formed being reduced by the stannous chloride with formation of the quadrantoxide and potassium stannate:[3]

$$4Cu(OH)_2 + 12KOH + 3SnCl_2 = Cu_4O + 6KCl + 3K_2SnO_3 + 10H_2O$$

Copper quadrantoxide is an olive-green powder which undergoes no change under water if the air be completely excluded. Exposed to air it rapidly absorbs oxygen. The composition of this compound is ascertained from the action of dilute hydrochloric or sulphuric acid upon it, when the following decomposition takes place:

$$Cu_4O + 2HCl = Cu_2Cl_2 + 2Cu + H_2O.$$
$$Cu_4O + H_2SO_4 = CuSO_4 + 3Cu + H_2O.$$

[1] Schweizer, *J. Pr. Chem.* 1857, **72**, 109.

[2] Lehmann, *Trans. Inter. Cong. Hygiene and Demography* (London), 1891, **5**, 63.

[3] Rose, *Pogg. Ann.* 1861, **120**, 1.

Copper Trientoxide, Cu_3O is prepared by heating cupric oxide at temperatures between 1,500° and 2,000° and forms a yellowish-red mass sufficiently hard to scratch glass. It is unaffected even by concentrated mineral acids with the exception of hydrofluoric acid but is dissolved by fused caustic potash.[1]

Copper Dioxide, $CuO_2 + H_2O$, is best obtained by allowing finely divided cupric hydroxide to stand with aqueous hydrogen peroxide in the cold for several days, the mixture being frequently shaken. A crystalline precipitate is thus formed, which, after washing with water, alcohol, and ether at 0°, is dried in vacuo. It has a yellowish-brown colour, and when moist readily decomposes above 6°; when dry it does not undergo change at 170°, but at 180° decomposes, forming cupric oxide.[2]

Cuprous Compounds.

158 *Cuprous Hydride* $(CuH)_n$.—This compound, discovered by Wurtz,[3] is deposited as a yellow or reddish-brown precipitate, when a solution of copper sulphate is treated with hypophosphorous acid at a temperature not exceeding 70°. The hypophosphorous acid may also be replaced by sodium or zinc hyposulphite.[4] At higher temperatures it decomposes into copper and hydrogen according to Wurtz, but according to Bartlett and Merrill[5] cupric hydride and hydrogen are really formed.

It readily ignites in chlorine gas and is decomposed by hydrochloric acid as follows:—

$$2CuH + 2HCl = Cu_2Cl_2 + 2H_2.$$

Cuprous Fluoride, CuF or Cu_2F_2, is best obtained by heating cuprous chloride in a current of hydrogen fluoride at 1100°—1200°, at which temperature the fluoride volatilises. It forms a ruby red crystalline mass, or red powder, which dissolves in boiling hydrochloric acid, but unlike cuprous chloride is not reprecipitated on addition of water.[6]

[1] Bailey and Hopkins, *Journ. Chem. Soc.* 1890, i. 269.
[2] Krüss, *Ber.* 1884, **17**, 2593. [3] *Compt. Rend.* 1844, **18**, 102.
[4] *Compt. Rend.* 1869, **69**, 196. [5] *Amer. Chem. Journ.* 1895, **17**, 185.
[6] Poulenc, *Compt. Rend.* 1893, **116**, 1446.

Cuprous Chloride, Cu_2Cl_2—This substance was first obtained by Boyle [1] by the action of copper on mercuric chloride. He compared the substance thus obtained, which he found turned green on exposure to air, to resin or gum, and hence he gave to it the name of *resina cupri* or *cuprum gummatosum*. Proust obtained the same compound by the action of the dichloride on the salts of the monoxide, and J. Davy showed that cuprous chloride is formed together with the cupric salt when copper foil or copper filings are thrown into chlorine gas, when they burn with the evolution of a red light. If hydrochloric acid be passed over hot copper contained in a glass tube this compound is formed, and is seen to condense in transparent drops (Wöhler). It may readily be prepared on the large scale by a number of methods, all of which consist eventually in the reduction of cupric to cuprous chloride. For this purpose a mixture of copper and cupric oxide may be boiled with strong hydrochloric acid, or a hydrochloric acid solution of cupric chloride with copper; the metallic copper may be replaced by zinc dust or the cupric chloride by a mixture of cupric sulphate and sodium chloride, and the reduction may also be effected by sulphur dioxide. In all cases the cuprous chloride remains dissolved in the excess of hydrochloric acid, but separates out on adding the solution to a large bulk of water, as a heavy white crystalline precipitate, which may be purified by washing. It crystallises from hot hydrochloric acid in white tetrahedra, has a sp. gr. of 3·7, and melts below a red heat, solidifying to a brown mass. Its vapour density both at a bright red and a white heat corresponds to the formula Cu_2Cl_2. On exposure to light the moist substance quickly assumes a dirty violet tint, but if dried in absence of air and light, it only assumes a faint yellow colour on exposure. When allowed to remain in moist air it absorbs oxygen and is converted into green cupric oxychloride. It dissolves readily in hydrochloric acid, and this solution absorbs carbonic oxide forming a compound which separates out in nacreous scales on saturating the concentrated solution with the gas. This has probably the composition $COCu_2Cl_2 + 2H_2O$, but as it so readily loses carbonic oxide, the formula has not been definitely ascertained. Cuprous chloride also readily dissolves in ammonia forming a colourless solution if air be completely excluded; this solution absorbs

[1] *Considerations and Experiments about the Origin of Qualities and Forms*, 1664.

carbonic oxide and also acetylene and other gaseous hydrocarbons belonging to the same series, and rapidly turns blue in the air owing to the absorption of oxygen and formation of cupric salts.

Cuprous Bromide, CuBr or Cu_2Br_2, is formed with ignition when bromine is brought into contact with copper heated below a red-heat. It forms a brownish crystalline mass which turns blue on exposure to sunlight and has a specific gravity of 4·72.

Cuprous Iodide, CuI or Cu_2I_2.—This is the only known iodide of copper. It is obtained by the direct combination of the two elements when heated together or when copper is dissolved in a hot concentrated solution of hydriodic acid. If potassium iodide be added to a solution of a cupric salt, cuprous iodide is precipitated, half of the iodine being liberated. The production of iodine can be prevented by the previous addition of sulphurous acid or ferrous sulphate :

$$2CuSO_4 + 2FeSO_4 + 2KI = 2CuI + Fe_2(SO_4)_3 + K_2SO_4.$$

Cuprous iodide is a white crystalline powder which undergoes little alteration on exposure to light, and has a specific gravity of 4·41. It melts at a red-heat, solidifying again to form a brown mass which yields a green powder.

159 *Cuprous Sulphide*, Cu_2S, occurs in nature as chalcocite, copper-glance, or vitreous copper in rhombic six-sided tables or prisms having a metallic lustre which is often tarnished green or blue, and has a blackish lead-grey streak. It has a specific gravity of from 5·5 to 5·8. The same compound is also formed as a black brittle mass when copper is burnt in sulphur vapour, and when large quantities of copper and sulphur are fused together. Mitscherlich in this way succeeded in obtaining this compound in rhombic octohedra. It is also formed when cupric sulphide is gently heated in a current of hydrogen, this method being frequently used for the gravimetric determination of copper.

Cuprous Sulphite, $Cu_2SO_3 + H_2O$.—This salt is obtained by passing sulphur dioxide into a hot solution of cupric acetate in acetic acid, and separates as a heavy white precipitate consisting of microscopic nacreous plates. It combines with the alkali sulphites forming a number of double salts, which are colourless crystalline compounds. The double ammonium salt $(NH_4)_2SO_3 + 2Cu_2SO_3$ when heated yields a bright red powder or scales of

cupro-cupric sulphite, $Cu_2SO_3 + CuSO_3 + 2H_2O$. A red modification of cuprous sulphite has also been described, but it appears not unlikely that this is also a cupro-cupric salt.

Cuprous Nitride, Cu_3N (?)—Nitrogen gas and ammonia do not act upon red-hot copper, the ammonia being simply decomposed into its elements. A nitrite may however be obtained by passing a current of ammonia gas over precipitated copper oxide at 250°, and forms a dark green powder, which at about 300° decomposes into its constituents with ignition.

Nitrocopper, $CuNO_2$ or $Cu_2(NO_2)_2$ is obtained as a maroon-coloured powder by passing pure and dry nitrogen peroxide over finely divided copper (obtained by the reduction of copper oxide), at 25–30°. It decomposes into copper and nitrogen peroxide at 90°, is violently attacked by water with evolution of nitric oxide and formation of cupric nitrite and nitrate, and when placed in ammonia gas becomes incandescent, with formation of water, ammonium nitrate and nitrite, copper and ammoniacal copper oxide remaining behind.[1]

Copper and Phosphorus.—These two elements unite together at a red-heat (Marggraf). When phosphorus is added to molten copper and the fused mass stirred up until it approaches its point of solidification, three distinct layers are formed. The uppermost layer consists of a bright, very hard, brittle mass which contains seven to twelve per cent. of phosphorus; the central layer, containing four to six per cent., is a grey granular mass, whilst the lowest, existing in only small quantity, contains about 0·5 per cent. of phosphorus. By melting these phosphides with copper, alloys containing any wished-for percentage of phosphorus may be obtained. These melt at a much lower temperature than pure copper even when the percentage of phosphorus is so low as 0·5.[2] The tenacity of the copper is also considerably increased by the presence of a small quantity of phosphorus, provided the metal be cast in a chill. Percy[3] has shown that the presence of a small quantity of phosphorus in copper has some effect in protecting the metal from the corrosive action of sea-water.

Cuprous Phosphide, Cu_3P, is formed when phosphuretted hydrogen is passed over heated cuprous chloride, or when phosphorus vapour is passed gently over ignited metallic copper.

[1] Sabatier and Senderens, *Compt. Rend.* 1892, **115**, 236; 1893, **116**, 756.
[2] Abel, *Journ. Chem. Soc.* 1865, 249.
[3] *Brit. Assoc. Reports*, 1849 [2], p. 39.

According to the temperature at which it is formed this compound is either black, or grey, or forms a silver white mass with metallic lustre. It is very brittle and when obtained at a high temperature it forms a coherent mass capable of taking a polish. It is scarcely soluble in hydrochloric acid but dissolves easily in nitric acid.

Cuprous Cyanide, Cu(CN) or $Cu_2(CN)_2$.—When a solution of potassium cyanide is added to a solution of copper sulphate a red precipitate of cupric cyanide is first formed; when the liquid is boiled cyanogen gas is given off and a white precipitate of cuprous cyanide deposited. This same compound is formed by the action of potassium cyanide on cuprous chloride, and dissolves in an excess of the reagent.

Cuprous Thiocyanate, Cu(CNS) or $Cu_2(CNS)_2$.—Potassium thiocyanate gives a black precipitate of cupric thiocyanate when added to a solution of copper sulphate. This on long standing and washing is converted into white cuprous thiocyanate. If a reducing agent such as ferrous sulphate or sulphur dioxide be present this latter compound is at once precipitated. This reaction is often employed for the separation of copper from other metals in quantitative analysis.

Cupric Compounds.

160 *Cupric Hydride*, CuH_2. This compound is obtained according to Bartlett and Merrill[1] by the action of heat on cuprous hydride. When freshly prepared it is a reddish-brown spongy mass, which changes after a time to a chocolate powder. It acts as a strong reducing agent, converting potassium chlorate in solution into the chloride, and the nitrate to nitrite and ammonia.

Cupric Fluoride, CuF_2. This salt is obtained by dissolving cupric oxide in hydrofluoric acid, and separates on evaporation in blue crystals having the composition $CuF_2 + 2H_2O$, which are sparingly soluble in cold water. They are decomposed at 100° with separation of the oxyfluoride, CuF(OH), and when heated with ammonium fluoride in a current of carbon dioxide, yield the anhydrous fluoride as a white amorphous powder, which becomes crystalline at 500° in an atmosphere of hydrogen fluoride.[2]

[1] *Amer. Chem. Journ.* 1895, **17**, 185.
[2] Poulenc, *Compt. Rend.* 1893, **116**, 1446.

Cupric Chloride, $CuCl_2$, is formed when metallic copper is burnt in an excess of chlorine, or when the hydrated crystalline chloride is heated. Cupric chloride is a dark liver-coloured powder which on heating is converted into cuprous chloride with loss of chlorine. It readily dissolves in water, forming a green liquid which is also obtained by dissolving the oxide or carbonate in hydrochloric acid. Rhombic prisms or needles having the composition $CuCl_2 + 2H_2O$ separate out on evaporation. The concentrated solution of the hydrated chloride has an emerald-green colour, and on dilution with water the colour changes to bluish-green. It is very deliquescent and is soluble in alcohol, the solution burning with a fine green flame and giving a characteristic channelled-space spectrum.

Basic Cupric Chloride, or *Copper Oxychloride*, $Cu_3O_2Cl_2 + 4H_2O = 2CuO + CuCl_2 + 4H_2O$. This compound falls down as a pale blue precipitate when caustic potash is added to an excess of a solution of cupric chloride. When the compound is heated it loses water and is converted into a brown or blackish powder, and when moistened, this takes up three molecules of water and changes again to a green colour. When a solution of cupric chloride is mixed with cupric hydroxide, or when sufficient caustic potash is added to the solution of the former salt to ensure complete precipitation, a compound having the composition $Cu_4O_3Cl_2 + 4H_2O$ is thrown down. This substance occurs native in the form of a green sand composed of small rhombic prisms found at Atacama, as well as in Peru, Bolivia, and other places, and hence termed atacamite. According to Field, this mineral is at the present day being formed on the south coast of Chili by the action of sea-water on copper pyrites. The same compound may be artificially obtained in the crystalline state by heating common salt with ammoniacal solution of copper sulphate to 100° (Debray), the decomposition being:

$$6NH_3 + 4CuSO_4 + 2NaCl + 3H_2O = 3(NH_4)_2SO_4 + Cu_4O_3Cl_2 + Na_2SO_4.$$

This compound is also formed when a solution of copper sulphate is boiled with a small quantity of bleaching-powder solution; the product obtained occurs in commerce as a light bright green powder, used in the arts as a pigment and known under the name of *Brunswick green*. On heating it loses water

and becomes black but regains the green colour on moistening. Other oxychlorides of copper are also known occurring partly as minerals and partly as artificial products. Cupric chloride also unites with other chlorides forming crystalline double salts.

Cupric Bromide, $CuBr_2$. When cupric oxide is dissolved in hydrobromic acid and the solution allowed to stand in a vacuum over sulphuric acid, the anhydrous bromide separates out in dark crystals very similar to those of iodine. These are very deliquescent and on heating in absence of air decompose into cuprous bromide and bromine.

Cupric Sulphide, CuS, occurs in nature as covellite or indigo-copper, occurring sometimes in hexagonal crystals but more frequently in the massive state as at Mansfeld, on Vesuvian lavas, and in Chili. It has a semi-metallic lustre, an indigo-blue colour and a specific gravity of 4·6.

This compound is prepared artificially by heating cuprous sulphide with flowers of sulphur to a temperature not above that of boiling sulphur (Hittorf). It also may be prepared by triturating finely-powdered cuprous sulphide in a mortar with cold strong nitric acid until the action ceases; the powder is then washed, cupric sulphide remaining behind.[1] It may likewise be obtained as a blackish-brown precipitate by passing a current of sulphuretted hydrogen gas into a solution of a cupric salt. The finely-divided moist precipitate easily oxidises on exposure to the air. When cupric sulphide is gently heated in absence of air or in a current of hydrogen, it decomposes into sulphur and cuprous sulphide, and this method is often used for the estimation of the metal (Rose).

Cupric Sulphate, $CuSO_4$. This salt, commonly termed copper sulphate, copper vitriol or blue vitriol, has long been known, being found in solution in the drainage water of copper mines. It was for a long time confounded with green vitriol or iron sulphate, this being partially due to the fact that both frequently occur together in the same drainage water and are capable of crystallising together. In the works attributed to Basil Valentine the fact is recognised that both iron and copper vitriol can occur together, for he says: "Venus and Mars can be brought back into a virtuous vitriol." The alchemists frequently experimented on such mixed vitriols, as they believed that they contained the *materia prima* employed for the preparation of

[1] Faraday, *Quart. Journ. Sci.* **21**, 183.

the philosopher's stone. Thus, in the above-mentioned work we read. "where copper and iron are found together gold will not be far distant."

The artificial production of copper sulphate is first described by Van Helmont in 1644, who obtained it by heating together copper and sulphur, and moistening the residue with rain-water. Glauber in 1648 proved that it may be readily obtained by boiling copper with oil of vitriol.

Copper sulphate is obtained on the large scale chiefly from copper pyrites, which is carefully roasted, the copper under suitable conditions being oxidised to copper sulphate whilst the iron is chiefly converted into oxide. The residue is lixiviated and the copper sulphate separated from the solution by crystallisation. The mother-liquors contain both copper and iron sulphates, from which the copper may be precipitated by scrap iron. For agricultural use the presence of iron in the copper sulphate is not injurious, and for sulphate intended for this purpose the mother-liquor may be directly evaporated. The precipitated copper as well as copper scale and metallic copper obtained by other processes or as scrap, is roasted in reverberatory furnaces and the product treated with dilute sulphuric acid. If the copper contains gold or silver it is treated with sulphuric acid mixed with its own volume of water, the silver and gold being left undissolved.

Where argentiferous copper ores are used the roasted ore is added in small quantities to sulphuric acid and digested until the solution contains but little free acid. Lead and gold remain behind as an insoluble powder, and the clear liquor is run into wooden tanks lined with lead, and containing strips of copper on which the whole of the silver and part of the arsenic and antimony are deposited, whilst the greater portion of the bismuth separates as a basic sulphate. The copper sulphate solution, thus freed from other metals is then crystallised in large lead-lined coolers, the crystals being deposited on strips of lead hung up in the liquid.

The commercial sulphate always contains small quantities of iron which may be removed by boiling the solution with a little nitric acid, the ferrous sulphate being thus converted into ferric sulphate which remains in the mother-liquor on recrystallisation.

Cupric sulphate is also obtained as a secondary product in the refining of silver; the silver is precipitated from a solution of

the sulphate in the metallic form by strips of copper and pure cupric sulphate remains behind.

Copper sulphate crystallises from warm saturated solutions on cooling in transparent blue asymmetric crystals (Fig. 80) having the formula $CuSO_4 + 5H_2O$ and a specific gravity of 2·28. 100 parts of water dissolve, according to Poggiale, as follows:—

	At 10°	20°	30°	50°	70°	90°	100°
$CuSO_4 + 5H_2O$	36·59	42·31	48·81	65·83	94·60	156·44	203·32.

The salt is insoluble in absolute alcohol and only slightly soluble in dilute spirits. When it is heated for some time to 100°, the hydrate $CuSO_4 + H_2O$ remains as a bluish-white powder, which at a temperature of from 220° to 260° loses an additional molecule of water leaving the anhydrous salt behind. This forms a white mass which is extremely hygroscopic, becoming blue on absorption of water. This reaction is sometimes used for the purpose of ascertaining the presence of water in organic liquids, and also for dehydrating the same. The anhydrous compound may be obtained in the form of grey prismatic needles by heating the hydrated sulphate with ammonium sulphate out of contact with the flame gases.[1].

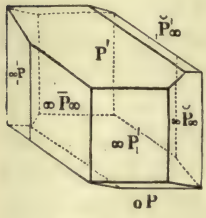
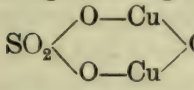


FIG. 80.

The anhydrous as well as the hydrated sulphate absorbs two molecules of hydrochloric acid gas with evolution of heat and formation of cupric chloride and sulphuric acid. This same decomposition takes place when copper sulphate is treated with an excess of aqueous hydrochloric acid; the temperature sinks and the salts dissolve with formation of a green liquid which on concentration yields crystals of cupric chloride. This reaction of copper sulphate is employed for separating hydrochloric acid from mixtures of gases, as for instance, from chlorine or from carbon dioxide which has been prepared by means of hydrochloric acid. Copper sulphate is largely used in calico-printing, and in the preparation of the pigments of copper, as Scheele's green and emerald green. It is also used in very large quantity in the processes of electro-metallurgy. A crude copper sulphate containing ferrous sulphate is used in agriculture for preventing "smut" in seeds.

Hydrates containing two and three molecules H_2O are also

[1] Klobb, *Compt. Rend.* 1892, **114**, 836.

known in addition to those described above, and copper also forms a series of basic sulphates. When the normal sulphate is kept for several hours at a dark red-heat, an amorphous orange-yellow powder remains behind having the composition  , which is decomposed in contact with cold water into copper sulphate and an insoluble green basic sulphate, $CuSO_4 + 3Cu(OH)_2$. By the action of boiling water a salt having the composition $CuSO_4 + 2Cu(OH)_2$ is formed. These as well as other basic salts are also obtained when a solution of copper sulphate is treated under certain conditions with potash or ammonia. Some occur as minerals; thus brochantite is a native basic sulphate having the formula $CuSO_4 + 3Cu(OH)_2$, and occurring in bright green rhombic tables. It can be artificially prepared by allowing a piece of porous limestone to lie in a solution of copper sulphate.

161 *Cupric Nitrate* $Cu(NO_3)_2$.—In his *De furnis novis philosophicis* published in 1648 Glauber mentions the fact that the solution of copper in nitric acid on evaporation leaves a green residue, and Boyle in 1664 observed that crystals can be obtained from the solution and that these have the power of colouring the flame of a spirit-lamp green. In order to prepare copper nitrate, copper scale or copper oxide is dissolved in dilute nitric acid and the solution evaporated to crystallisation. In this way fine blue prismatic crystals, having the composition $Cu(NO_3)_2 + 3H_2O$ are obtained which possess a caustic metallic taste and cauterise the skin. At a low temperature the salt crystallises with six molecules of water. The anhydrous nitrate is not known, as the hydrated salt when heated to 65° begins to lose nitric acid, a basic salt having the composition $Cu(NO_3)_2 + 3Cu(OH)_2$ being formed. Copper nitrate is deliquescent and very soluble in water, and is deposited as a fine crystalline powder when its concentrated solution is mixed with nitric acid of specific gravity 1·522. This salt, owing to the ease with which it is decomposed, possesses strong oxidising properties. If some crystals of it be wrapped up in tinfoil and rubbed, decomposition begins, often accompanied by a rise of temperature sufficient to cause emission of sparks. If a solution of copper nitrate be evaporated with one of ammonium nitrate, decomposition takes place at a certain degree of concentration attended with violent detonations. Copper nitrate is used as

an oxidising agent in the processes of dyeing and calico-printing, especially in the production of catechu-browns, and in some steam colours containing logwood.

Cupric Phosphide, Cu_3P_2, is formed when phosphuretted hydrogen is passed over cupric chloride or by passing the same gas into a solution of copper sulphate, as well as when phosphorus is boiled with a cupric salt. Cupric phosphide is a black powder, or, when prepared at a high temperature, a greenish black metallic mass which, when ignited in hydrogen, is converted into cuprous phosphide.

In addition to the cuprous and cupric phosphides, a number of others have been described. The compound Cu_5P_2 crystallises in hard steel-grey hexagonal prisms, and CuP forms a grey crystalline powder.[1]

Normal Cupric Phosphate, $Cu_3(PO_4)_2+3H_2O$, is best obtained by dissolving the carbonate in dilute phosphoric acid and heating the solution to 70°, when a fine blue crystalline powder is deposited. On heating this with water in closed tubes it decomposes into phosphoric acid and a *basic salt* $PO_4\left\{\begin{matrix}Cu\\CuOH\end{matrix}\right.$ (Debray), which latter occurs in nature as libethenite. The artificial compound crystallises in rhombic prisms, and libethenite in dark olive-green prisms having a waxy lustre. The same compound also occurs in the massive state.

Another basic copper phosphate is the mineral phosphochalcite or pseudomalachite; this occurs in asymmetric emerald-green crystals having the composition $PO_4(CuOH)_3$. Other basic phosphates of copper are known.

Copper Arsenides.—These elements combine in several proportions, whilst certain copper arsenides are found as minerals; thus whitneyite, Cu_9As, occurs as a bluish red or greenish white amorphous or crystalline malleable substance found in Michigan and also in California and Arizona. Algodonite, Cu_6As, found in Chili and Lake Superior, possesses a silver-white or steel-grey lustre; and domeykite, Cu_3As, found at Portage Lake, has a tin-white to steel-grey colour. According to Reinsch the grey deposit obtained when metallic copper is placed in a solution of arsenious oxide in hydrochloric acid has the composition Cu_5As_2, and this on heating is converted into Cu_3As. When equal parts of arsenic and copper filings are fused together, a white finely granular alloy termed white

[1] Granger, *Compt. Rend.* 1891, **113**, 1041; 1893, **117**, 231.

copper is formed, having the composition Cu_4As. When arseniuretted hydrogen is passed over dry cupric chloride the alloy Cu_3As_2 is formed.

Cupric Arsenite, $CuHAsO_3$, was first obtained by Scheele by precipitating a solution of potassium arsenite with copper sulphate, and is still prepared by the same process. It is a siskin-green precipitate, which is known as a pigment under the name of *Scheele's green*. The salt dissolves in caustic potash with a blue colour and is then quickly decomposed on heating with separation of copper oxide.

Arsenates of Copper.—These salts correspond closely to the phosphates. Several basic salts occur in the mineral kingdom. The *ortharsenate* $Cu_3(AsO_4)_2+2H_2O$ is obtained as a blue amorphous powder by heating together copper nitrate and calcium arsenate. Olivenite, $AsO_4\begin{cases}Cu\\CuOH,\end{cases}$ crystallises in olive-green or brown rhombic prisms, and can be obtained artificially by heating a solution of the ortharsenate to 100°.

Clinoclasite, $AsO_4(CuOH)_3$, forms dark green monosymmetric prisms possessing a pearly or vitreous to resinous lustre.

162 *Carbonates of Copper.*—We are only acquainted with basic copper carbonates. Of these two occur in large quantity in the mineral kingdom. Malachite, $CuCO_3+Cu(OH)_2$, forms monosymmetric, frequently twin, crystals which are rarely perfectly developed, simple crystals being seldom found. It also occurs massive with botryoidal or stalactitic surface, often fibrous and frequently granular or earthy. Its colour is a bright green, and its specific gravity varies from 3·7 to 4·01. Green malachite accompanies other ores of copper, occurring especially in the Urals, at Chessy in France, in Cornwall and Cumberland in England, and at the copper-mines of Nischne-Tagilsk. The fibrous varieties are frequently deposited in different coloured layers which take a high polish, and from these masses vases and other ornamental articles are manufactured. It also forms a most valuable copper ore. Crystals of malachite can be obtained artificially by allowing a piece of porous limestone to lie in a solution of copper nitrate having a specific gravity of 1·1, until the stone becomes covered with basic nitrate and then bringing it into a solution of sodium carbonate having a specific gravity of 1·04, when after a few days malachite crystals are formed (Becquerel). When a solution of copper sulphate is precipitated in the cold with sodium carbonate, a blue precipitate of

$CuCO_3+Cu(OH)_2+H_2O$ is thrown down. This on standing is converted into a green powder having the composition of malachite. Verdigris or copper rust formed by the joint action of air and water on copper possesses the same composition as malachite.

Azurite or *azure copper ore*, $2CuCO_3+Cu(OH)_2$, occurs together with malachite and other copper ores in shining monosymmetric tables or short prisms, and also as an amorphous or earthy mass having a dark azure-blue colour. It possesses a specific gravity of 3·5 to 3·83. If crystallised copper nitrate be heated with pieces of chalk under a pressure of from 3 to 4 atmospheres a crystalline warty mass of azurite is formed (Debray). Azurite dissolves in a hot solution of sodium bicarbonate and the solution on boiling deposits a green powder of malachite.

163 *Silicates of Copper.*—Two silicates of copper occur as minerals. *Dioptase* or *emerald copper*, H_2CuSiO_4, is found in compact limestone in the Kirghese Steppes and also in Siberian gold-washings. It forms emerald-green crystals, assuming tetratohedral forms of the rhombic system and having a specific gravity of 3·3.

Chrysocolla, $H_2CuSiO_4+H_2O$, exists as a bluish botryoidal mass occurring with other copper ores. The name of chrysocolla occurs in old writers and serves to describe the most diverse bodies. The word originally was used to signify the substance employed for soldering gold (*χρυσός*, gold, and *κολλάω*, to cement); and this being prepared from urine was probably microcosmic salt which became coloured blue in the act of soldering gold to copper or brass. The word then came to be used for any green or blue substance, especially such as contained copper; the confusion thus created was great, all blue or green minerals, such as emerald and malachite, as well as substances which were employed for soldering, being termed chrysocolla. Brochant, in the year 1808, first proposed to confine the use of this name to the particular mineral.

Ammoniacal Compounds of Copper.

164 By the action of ammonia on both cuprous and cupric salts, a large number of compounds have been obtained, the empirical formulæ of which show that combination has taken place

between the copper salt and a varying number of molecules of ammonia. As to the manner in which the combination takes place, and the exact constitution of the products, very little is at present known, and they are usually formulated as additive compounds. Many other metals form similar series of ammoniacal derivatives, these being often more complex than in the case of copper, as for example with cobalt and platinum. The compounds appear to be formed chiefly by the metals occurring in the middle of Mendeléeff's double periods (p. 48).

The ammoniacal cuprous compounds are colourless when pure but very readily undergo oxidation, yielding the corresponding ammoniacal cupric salts, which usually have a deep blue colour and yield solutions of the same colour. The most important of these are the derivatives of cupric chloride and sulphate.

Cupric Chloride and Ammonia.—Anhydrous cupric chloride absorbs ammonia, increasing in bulk and forming a blue powder having the composition $CuCl_2+6NH_3$. When ammonia is passed into a hot saturated solution of cupric chloride a dark blue solution is formed, which on cooling deposits small dark blue octohedra or pointed quadratic prisms of *cuprammonium chloride*, $CuCl_2+4NH_3+H_2O$. Both compounds are converted at 150° into the compound $CuCl_2+2NH_3$, which is a green powder, and on further heating decomposes as follows:

$$6(CuCl_2+2NH_3)=3Cu_2Cl_2+6NH_4Cl+4NH_3+N_2.$$

Water converts it into cuprammonium chloride, ammonium chloride, and a basic cupric chloride having the composition $CuCl_2+4CuO+6H_2O$.

Cupric Sulphate and Ammonia.—When a solution of copper sulphate is treated with ammonia a basic sulphate is first thrown down. On further addition of ammonia this dissolves to a deep pure blue liquid containing *cuprammonium sulphate* $CuSO_4+4NH_3+H_2O$, which was first described by Stisser in 1693 as an *arcanum epilepticum* and afterwards termed *cuprum ammoniacale*. In order to obtain this compound in fine crystals a layer of strong alcohol is poured on to the concentrated aqueous solution and the whole allowed to stand: in this way azure-blue transparent very long and thin rhombic prisms are deposited. These on exposure to the air lose ammonia and are gradually transformed into ammonium sulphate and basic copper

sulphate. Heated gently to 150° an apple-green powder of the composition $CuSO_4+2NH_3$ is obtained. Anhydrous copper sulphate absorbs dry ammonia gas with evolution of heat, forming a fine blue powder consisting of $CuSO_4+5NH_3$, which like the foregoing compound on heating to 200° forms the compound $CuSO_4+NH_3$ (Graham).

It will be noticed that in several of these compounds the total number of molecules of water and ammonia in combination with the copper sulphate molecule is five, and they may therefore be regarded as crystallised copper sulphate, $CuSO_4+5H_2O$, in which either the whole or a certain number of the water molecules have been replaced by an equal number of ammonia molecules. The same relation is found still more prominently with the ammoniacal compounds of some of the other metals.

Detection and Estimation of Copper.

The halogen compounds and nitrate of copper colour the non-luminous gas flame green, and the same coloration is obtained from the other salts when mixed with a chloride or moistened with hydrochloric acid.

The spectrum of this flame is a banded one containing a large number of lines of which two in the violet lying between the rubidium and cæsium lines are the most characteristic. The spark spectrum of cupric chloride is also rich in lines and contains very bright lines in the green (Lecoq de Boisbaudran). When borax is moistened with any copper salt and heated in the oxidising flame a bead is obtained which, when hot, is green and when cold possesses a blue colour; in the reduction flame, especially with the addition of a small quantity of tin or tin compound, the bead becomes red and opaque with separation of cuprous oxide or metallic copper. Copper salts are thrown down by sulphuretted hydrogen in the form of a brownish-black precipitate of cupric sulphide, CuS, which is slightly soluble in ammonium sulphide, but not in freshly prepared potassium or sodium sulphide. The precipitated sulphide dissolves readily in warm dilute nitric acid forming a clear blue solution which assumes a fine dark blue colour on the addition of ammonia. This reaction is employed for the quantitative separation of copper from all other metals. Copper can also easily be detected

by the reduction to the red metallic bead on charcoal before the blowpipe, or upon the charred end of a lucifer match (Bunsen's test).

Copper is determined quantitatively either as oxide, sulphide or metal. For the purpose of determining it as oxide, the boiling solution of the copper salt is treated with a slight excess of pure potash or soda, the precipitate repeatedly washed by decantation with boiling water, then thrown on to a filter, again washed, dried, and ignited. When copper is determined in the metallic state the solution must be free from nitric acid; this is attained by evaporating repeatedly with hydrochloric acid or sulphuric acid; the solution is then brought into a platinum basin, a small quantity of zinc added, and enough hydrochloric acid to set up a slow evolution of hydrogen. The copper separates out partly as a solid deposit on the platinum and partly in the form of a spongy mass. When the whole is thrown down and the zinc is all dissolved, the copper sponge is pressed into a coherent form, washed repeatedly by decantation with boiling water, dried in a steam-bath, and weighed together with the tared basin. As pure zinc is not always easy to obtain, cadmium or magnesium may be employed instead. Very satisfactory results are obtained by the electrolytic deposition of the metal, this method being especially advantageous where a large number of determinations have to be made daily as is the case in a copper works.

Atomic weight of Copper.—By the reduction of precipitated copper oxide with hydrogen Berzelius obtained the number 62·83, whilst Erdmann and Marchand by the same method obtained the number 62·98. Hampe, by the reduction of the oxide and by the electrolysis of pure copper sulphate, obtained a number almost identical with that of Berzelius, viz., 62·85. The recent careful experiments of Richards have shown that all these numbers are too low, the error being due to the fact that copper oxide contains occluded nitrogen and oxygen, and that copper sulphate cannot, as previously supposed, be completely dehydrated at 255°. Richards therefore determined the atomic weight by the analysis of pure cupric bromide, the amount of silver required for complete decomposition of the bromide and also the weight of the bromide formed being ascertained. The average of the results gave the number 63·168 for the atomic weight of copper if silver = 107·13 and oxygen = 15·88. From the determination of the copper and of the sulphuric acid in copper

sulphate he obtained the number 63·139, and from the average of the five most trustworthy series of experiments concludes that the atomic weight is 63·137.[1]

SILVER (ARGENTUM), Ag = 107·13.

165 Silver has been known from the earliest times, and the oldest names by which it was designated referred to its bright white colour; thus in the Hebrew, Késeph, the root signifies to be pale, whilst the Greek word ἄργυρος, silver, is derived from ἀργός, shining. The alchemists termed silver Luna or Diana, and it is often represented by the symbol of the crescent moon.

Silver occurs frequently in the native state, and is sometimes found in considerable quantity; thus, in the museum at Copenhagen is a mass of native silver found at Kongsberg in Norway which weighs a quarter of a ton, and in South Peru masses have been found which weigh more than 8 cwt., whilst at Idaho, at the "poor man's lode" large masses of native silver have also been obtained. Native silver usually contains gold, copper, and sometimes mercury and other metals.

The most important ores of silver are: argentite or silver-glance, Ag_2S; pyrargyrite, ruby-silver, or dark-red silver, Ag_3SbS_3; stromeyerite or silver-copper glance, $(AgCu)_2S$; stephanite, Ag_5SbS_4; polybasite, $(AgCu)_9(SbAs)S_6$; chlorargyrite or horn-silver, AgCl. Of less importance are proustite or light-red silver ore, Ag_3AsS_3, dyscrasite, Ag_4Sb, silver bromide, AgBr, silver iodide, AgI, and others. Silver also occurs in sea-water, a fact which was known to Proust in the year 1787.

Metallurgy of Silver.—Metallic silver is prepared from its ores according to three different processes; either it is alloyed with lead and then the lead removed by oxidation, or it is amalgamated with mercury and this removed by distillation; or lastly, it is brought into solution as a salt and the metal precipitated by means of copper. The practical adoption of one or other of these processes depends upon the nature of the ore, the position of the mine, and the price of labour, fuel, &c.

It was by the first of these methods that the ancients extracted silver from its ores, and this one remained for long the

[1] Numerous papers in *Chem. News*, 1891-2, **63, 65, 66.**

only known process. Strabo describes the method adopted in Spain for this purpose. The washed ore was melted with lead and after this was got rid of (*ἀποχυθέντος τοῦ μολύβδου*) the pure silver remained behind. Pliny also, though he did not understand the nature of the operation, states that in order to obtain pure silver the ore must be cupelled together with lead; concerning the silver ore he says, "excoqui non potest, nisi cum plumbo nigro aut cum vena plumbi—et eodem opere ignium descendit pars in plumbum, argentum autem innatat, ut oleum aquis," being an indistinct statement of the mode in which metallic silver separates from the oxidised slag. This process was termed in the works attributed to Basil Valentine "Saigern" or "eliquation."

The Cupellation Process.—In this process the silver ores are first converted into an alloy of lead and silver by heating with the former metal, which reduces the silver to the metallic state, the excess of lead combining with it to form an alloy. The metallic lead obtained from galena always contains silver in small quantities, and from this a quantity of lead rich in silver is obtained by liquation, according to Pattinson's process. (See under Lead.) To obtain the silver free from lead in both cases the alloy is subjected to the process of cupellation, the lead being oxidised to litharge, which is removed, leaving the silver in the metallic state. For this purpose there are many distinct forms of furnace, modes of refining, &c., in use, but only two distinct methods of cupellation are employed, viz.: (1) the English, and (2) the German system.

(1) *The English Process.*—The peculiarity of this system is that the cupel or porous hearth upon which the oxidation takes place is movable, the lead being added at intervals.

Figs. 81 to 85 inclusive, show the construction of the English cupellation furnace or refinery. Fig. 81 shows the side-elevation; Fig. 82, the plan; Fig. 84, a transverse section in the line A B; Fig. 83, a transverse section in the line C D, and Fig. 85, the plan of the test and test frame.

The refinery consists essentially of a reverberatory furnace. The metal to be refined is placed upon the hearth, or cupel, or test (E), which consists of an oval wrought-iron frame (A A′ Fig. 85) about five feet long and two and a half feet wide, crossed by five iron bars (*a*). This frame is filled with finely-powdered bone-ashes, moistened with a little water in which a small quantity of potassium carbonate has been dissolved.

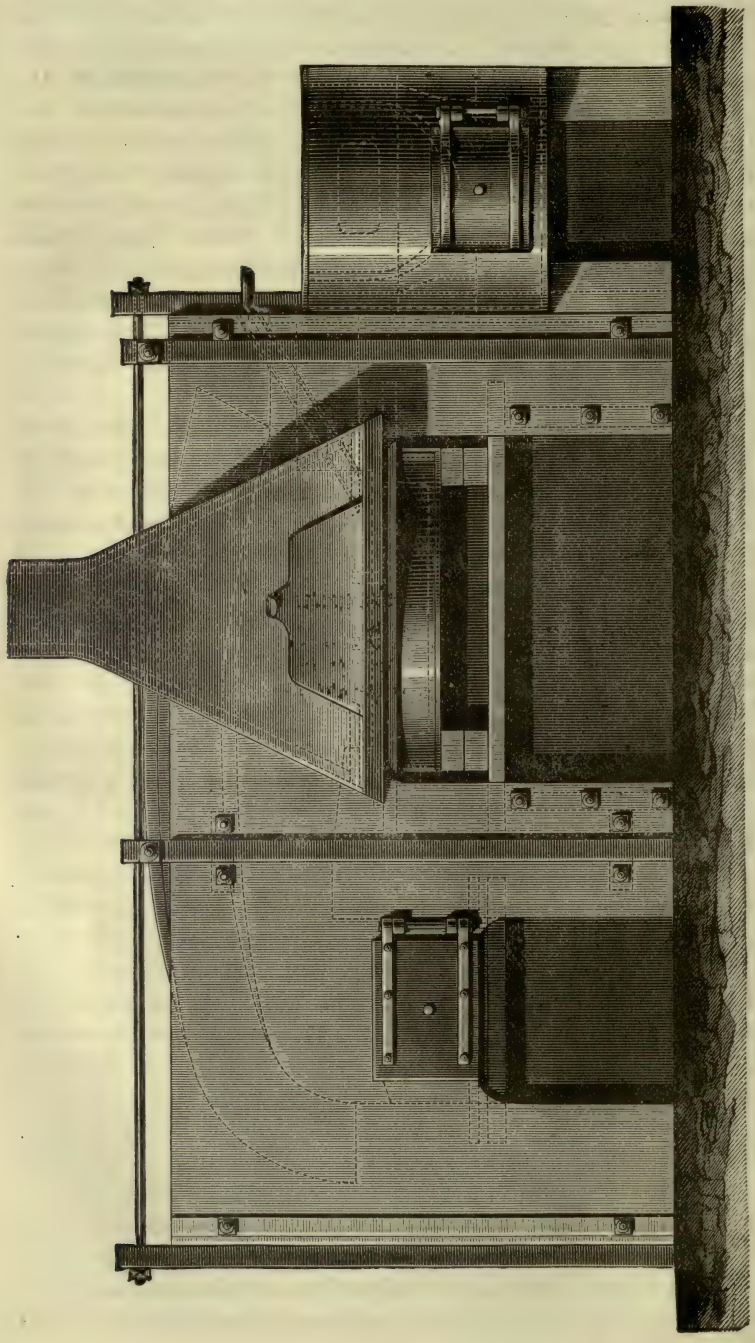


FIG. 81.

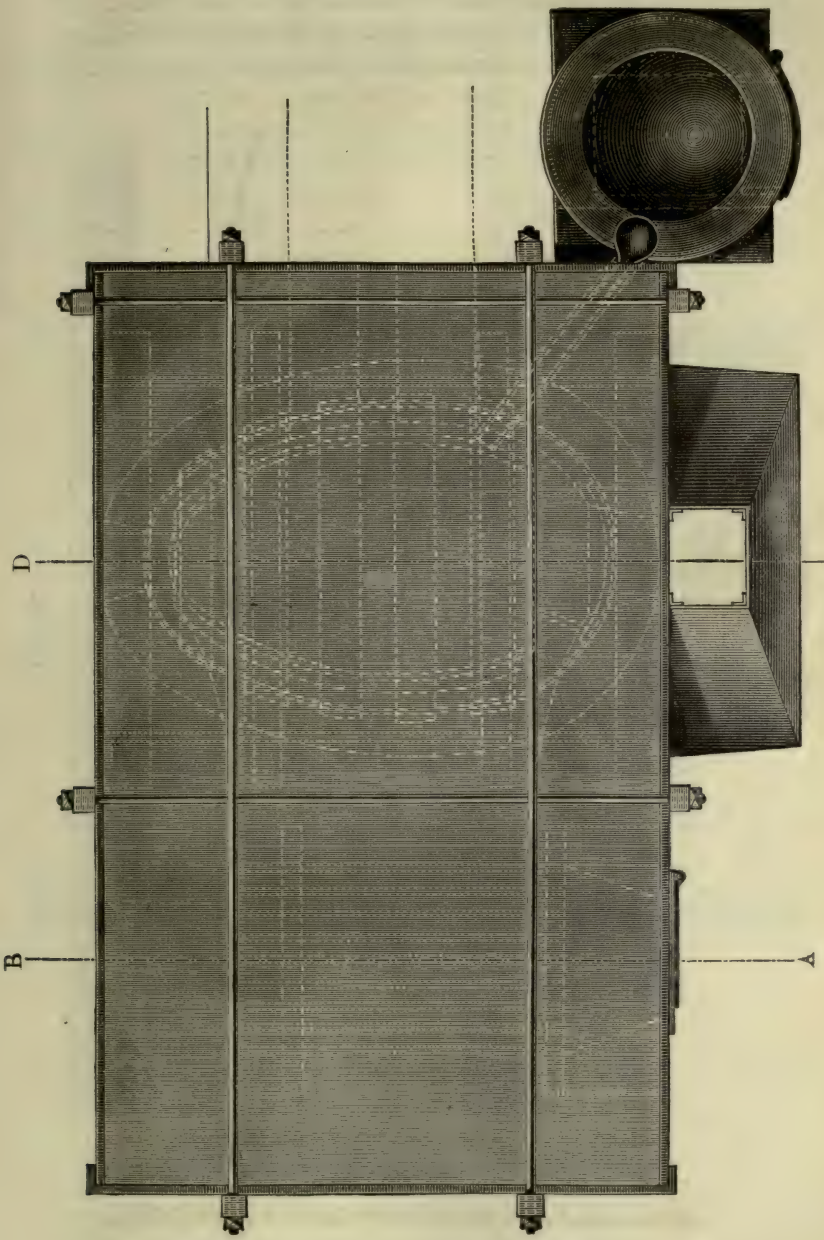


FIG. 82.

This is well solidified by beating, and scooped out until it is about an inch thick and has the form shown in the figure. A flat rim of bone-ash is thus left all round, about two inches wide, except at one end (E), called the front or breast of the cupel where

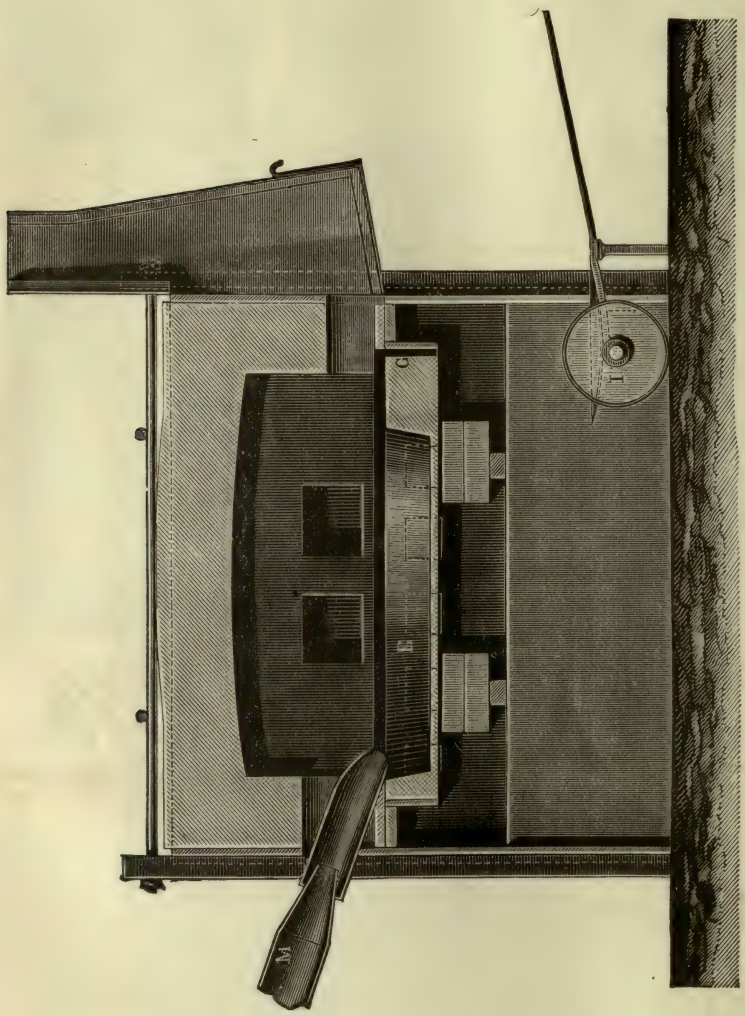


Fig. 83.

it is five inches wide, and through this a channel (G) connecting the bed of the cupel with the slot (G′) is cut to allow the melted oxide of lead to flow out into the wagon (I), beneath, without coming in contact with the iron, which it would corrode. The

cupel thus arranged is wedged up into its place in the furnace, of which it forms the hearth (E), where it is so arranged that the flame from a coal fire lying on the bars plays over its surface, the door of the furnace being shown in Fig. 81, and the products of combustion escape through two flues. A blast of air from the nozzle or tuyere (M Fig. 83), enters the cupel at the side opposite that against

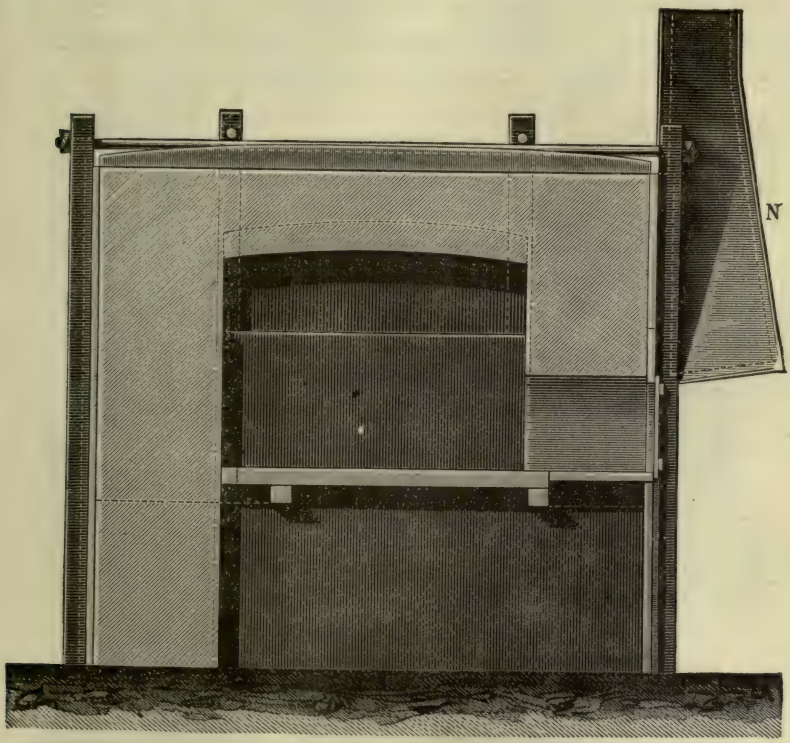


Fig. 84.

which the breast of the cupel is placed, a current of air being thus blown over the surface of the lead at the rate of about 200 cubic feet per minute. Opposite the door is a hood (N) for carrying the fumes into the chimney. The temperature of the cupel is gradually raised to redness, and it is almost filled with the lead to be heated, which is ladled in from the iron pot where it has been previously melted by means of a fire placed beneath. Fresh lead is added from time to time to supply the

place of that which is oxidised, until at length a quantity of lead originally amounting to about five tons is reduced to between two and three cwt. This melted metal is withdrawn by making a hole through the bottom of the cupel; the aperture is afterwards closed with fresh bone-ash, and another charge is proceeded with. When a quantity of rich lead sufficient to yield from 3,000 to 5,000 ounces of silver, or from 93 to 155 kilos., has been thus obtained, it is again placed in a cupel, and the last portions of lead are removed. It is found advantageous to effect this final purification of the concentrated silver-lead separately, because in the last stages of the operation the

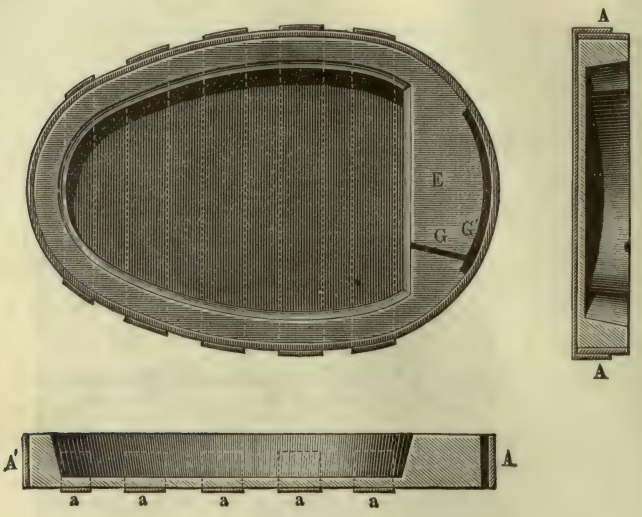


Fig. 85.

litharge carries a good deal of silver down with it; these portions of litharge, therefore, on being reduced, are again subjected to the desilverising process.

(2) *The German Cupellation Process.*—This differs from the English inasmuch as the hearth is formed of clay instead of bone-ash. It is made of large dimensions, and the whole of the charge is placed on the cupel at once. The furnace used for this purpose is shown in Fig. 86. The circular cover *k*, is movable for the purpose of renewing the cupel. When all is ready, straw is thrown upon the hearth, on to which the pigs of rich lead are placed; the cover *k* is then lowered and the joints made good with clay; the fire is lighted, and as soon as the lead is melted

its surface becomes covered with a dark crust termed "abzug," consisting of the oxides of foreign oxidisable metals and other impurities in the lead; this crust is skimmed off through the working door (*g*); the heat is then kept so as to maintain the lead at a dark-red heat, until the impurities cease to separate in the form of the scum. The next product which appears is known as "abstich," or impure litharge, and at the end of two hours the formation of the pure litharge begins, the temperature being kept up at a cherry-red heat until the operation is complete. Just before the last portions of lead are removed a

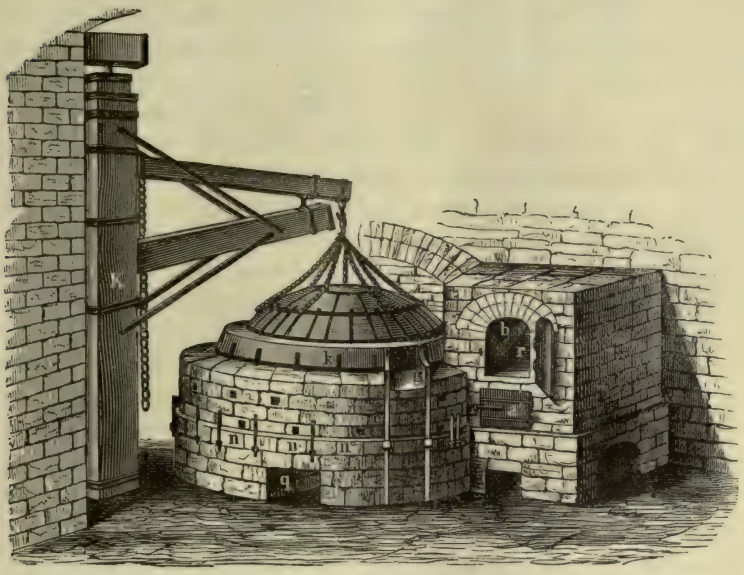


FIG. 86.

beautiful appearance, known as the fulguration of the metal, is noticed. During the early stages of the operation the film of lead oxide is constantly being formed, and this is renewed as rapidly as it is removed; but when the lead has all been oxidised, the film of litharge becomes thinner and thinner, and as it flows off a succession of beautiful iridescent tints due to the colour of thin films (Newton's rings) is observed, and after a few moments the film of oxide suddenly disappears and the brilliant surface of the metallic silver is seen beneath.

To obtain the silver from the alloy of zinc, silver and lead obtained in the Parkes process for desilverising lead (see Lead),

this is first heated slightly above the melting point of lead to remove as much of the latter as possible, and the residue heated with lime and coal in a retort just as in the Belgian process for the manufacture of zinc. The residual lead-silver alloy is then cupelled in the usual manner.

The Mexican Amalgamation Process.—Although the ancients were well acquainted with the fact that mercury dissolves gold and silver, it does not appear that they applied this knowledge to the extraction of silver from its ores. This was first done in Mexico in the year 1557 by Bartholomeo de Medina, and applied on the large scale in the year 1566. The same process was employed at Potosi in Peru in 1574, and fully described in 1590 by Joseph Acosta, in his *Historia natural y moral de las Indias.* The identical method is still carried on in Mexico, Peru, and Southern Chili, and is valuable for those localities where cheap fuel cannot be obtained. The ores which are worked by this process contain metallic silver, sulphide of silver, chloride of silver, &c., these substances being distributed in small masses through large quantities of gangue, thus rendering it difficult or impossible to separate the ore by washing.

The first operation in the process, which has to be carried on in a country devoid of fuel and running water, and where, therefore, neither steam nor water-power can be obtained, is the fine division of the ore. This is effected by stamping and grinding mills worked by horse or mule power, and termed *arrastra.* Into these water and ore are brought and ground together to a fine mud between blocks of porphyry fastened to an axis which is turned by the mules; the wet and powdered ore is then brought on to a paved floor termed a *patio,* and mixed with from 3 to 5 per cent. of common salt, and the salt thoroughly incorporated with the mass by the treading of mules. After standing for a day, mercury is added together with a substance termed *magistral,* an impure mixture of cupric and ferric salts. As soon as the magistral has been added, more mercury is poured on, and the heap or *torta* is again trodden by mules to bring about a thorough incorporation of the ingredients and thus to effect the chemical decomposition which their contact entails. The treading of the torta is generally performed by mules which are blindfolded and tied together four abreast; one mule for every two montones (about three tons) is required at Guanaxuato for the effectual treading of a heap. A driver, who stands in the centre of the torta, guides the animals with a long halter,

causing them first to tread at the outer edge, and gradually diminishing the radius of the circle described. The time necessary for working a torta varies from fifteen to forty-five days according to circumstances (Phillips).

As soon as the amalgamation is found to be complete, the slimy mass is washed in buddles worked by mules, the lighter particles of mud washed away and the heavier amalgam deposited. The amalgam is next filtered through canvas bags to remove mechanical impurities, and then distilled by being placed under a large iron bell luted at the bottom with water, round the upper part of which a charcoal fire is lighted. The silver which is then left behind, and termed *plata piña*, possesses a white frosted appearance and is fused into bars in the usual way.

The chemical reactions which occur in the process have been investigated by Boussingault, Karsten, and other chemists, but in spite of their investigations there still remains some degree of doubt respecting the exact nature of the reaction.

The following is the probable explanation of the chemical changes which occur. The first reaction is a double decomposition between the sulphates of iron and copper and chloride of sodium with formation of the chlorides of the metals. These decompose silver sulphide into silver chloride:

$$2CuCl_2 + Ag_2S = Cu_2Cl_2 + 2AgCl + S.$$

The cuprous chloride then formed dissolves in common salt and acts further upon the sulphide:

$$Cu_2Cl_2 + Ag_2S = Cu_2S + 2AgCl.$$

The solution of the silver chloride in common salt is then decomposed by the metallic mercury with formation of calomel and metallic silver. All the mercury which is thus converted into calomel is lost, and it amounts to about double the weight of the silver obtained.

The American or *Washoe Amalgamation Process.*—Owing to the scarcity of fuel and labour in the Nevada districts, where large quantities of both rich and poor silver ores occur, it is found impossible to work the ordinary methods, because a process necessitating the preliminary roasting of the ore cannot be carried on, and the loss of mercury in the Mexican process is too great to render that method applicable to the large quantity of poor ore which the district yields.

This necessity has led to the invention of a process of amalgamation in iron pans, which is called, from the name of the district, the Washoe Process. The richer ores of the Nevada mines contain many other metals, and are usually roasted with common salt in reverberatory furnaces and then amalgamated in barrels. The poor ore, on the other hand, after having been stamped to powder is then ground in cast-iron pans together with mercury and hot water, with or without the addition of common salt and copper sulphate. The amalgam is next washed, strained in bags, and distilled in carefully-constructed cast-iron retorts, and the silver which remains melted and cast into ingots. The chemical changes which occur in this process of amalgamation are similar to those taking place in the Mexican operation, but as the ore contains a considerable proportion of native silver, the presence of a copper salt is not so necessary, as under the influence of heat and friction mercury and iron alone are capable of extracting the silver. The loss of mercury in the Washoe method is much less than in the older amalgamation operations, as it is chiefly mechanical, no mercury salt being formed.

Another improvement is the addition of from 1 to 2 per cent. of sodium to the mercury whilst the amalgamation is going on. This depends upon the fact that pure mercury becomes covered with a coating of mercury sulphide which divides the metal into fine globules or makes it "mealy"; the addition of sodium prevents this, as the alkali-metal decomposes the sulphide of mercury with formation of sulphide of sodium and enables the mercury to flow together into a coherent liquid mass.

166 *Extraction of Silver in the Wet Way.*—Several of these processes have now come into general adoption in Europe. *Ziervogel's process,* now carried on in Saxony (see p. 314), depends upon the fact that when argentiferous copper pyrites is roasted, the copper and iron sulphides are converted into insoluble oxides, whilst the silver is converted into a soluble sulphate which is dissolved out by lixiviating the roasted ore with hot water, the silver being precipitated from this solution in the metallic state by treatment with metallic copper.

Percy-Patera Process.—Another wet process in use at Joachimsthal depends upon the following reactions, first suggested by Percy, and afterwards carried out by von Patera. The argentiferous ore is first roasted with common salt, by which the silver is converted into the chloride; this is then dissolved out

by a cold dilute solution of sodium thiosulphate, the silver in solution being precipitated as sulphide by sulphide of sodium; lastly the sulphide of silver is reduced to metal by exposure to a high temperature in a muffle furnace.

Augustin's Process.—This method is chiefly employed for argentiferous copper regulus, but may also be used for argentiferous ores. These are roasted to remove excess of sulphur, and then heated with 5 per cent. of common salt, and the silver chloride thus formed extracted by a hot saturated solution of the same, and the silver deposited from the solution by the action of metallic copper.

Claudet's Process.—The burnt pyrites of the sulphuric acid makers not only contains, as we have seen, copper, but also small quantities of silver, which occurs in the cupreous liquors in the form of chloride dissolved in the excess of common salt. Although the quantity of silver in the burnt ore does not often exceed 12 dwts. to the ton, it is found possible to obtain this economically in the form of insoluble silver iodide by adding a solution of potassium iodide to the tank liquor, a small trace of gold being at the same time precipitated. The results obtained at the Widnes metal-works by this process show that 0·65 oz. of silver and 3 grains of gold may be extracted from each ton of ordinary Spanish pyrites.

The total production of silver during 1892 throughout the world is given in the following table expressed in kilos.:[1]

United States of America	1,804,377	France	71,117
Australia	418,087	England	6,156
Mexico	1,419,634	Canada	9,797
Russia	13,234	Argentine	14,918
Germany	168,768	Columbia	31,232
Austria-Hungary	52,020	Bolivia	372,666
Sweden and Norway	9,323	Chili	70,794
Italy	27,583	Peru	74,879
Spain	51,502	Central America	48,123
Turkey	1,323	Japan	43,282
			4,708,815

167 *Preparation of Pure Silver.*—The purest silver which occurs in commerce contains traces of other metals. Stas'

[1] *Tech. Chem. Jahresber.* 1894, 341.

classical researches on atomic weight determinations have shown how difficult it is to obtain any substance chemically pure, and this fact is especially well illustrated in the case of silver, a metal which possesses such characteristic reactions that one would suppose its separation in a state of chemical purity to be an easy task, and yet this is far from being the case. The best method for obtaining pure silver is to dissolve ordinary silver in pure nitric acid, when a certain quantity of gold remains undissolved. The solution is then evaporated, and the residue fused in order to decompose any platinum nitrate that may be present. The residue is next dissolved in dilute ammonia, and the filtered blue liquid diluted with enough water to bring the strength down to 2 per cent. of silver. A sufficient quantity of normal ammonium sulphite is now added to render the solution colourless on warming, and the liquid is allowed to stand in close stoppered vessels for twenty-four hours, when a third of the silver separates out in the crystalline form. The liquid, which is still blue when cold, is poured off and heated from 60° to 70°, when the remainder of the silver is deposited. In order to remove every trace of copper, the metallic precipitate is washed with water and allowed to stand for several days in contact with strong ammonia; it is then again washed and dried and fused in an unglazed porcelain crucible with 5 per cent. of fused borax and 5 per cent. of sodium nitrate, and lastly it is cast in moulds which have been lined with a mixture of burnt and unburnt porcelain clay. The bars must then be cleaned with sand and heated with potash to remove every trace of adherent silicate, and finally washed with water.

Stas also prepared the pure metal from the commercial fine silver as follows. It is first dissolved in dilute nitric acid, and the evaporated residue fused as long as red fumes are evolved. The mass is then dissolved in water, filtered and diluted with thirty parts of distilled water to one of silver, the silver chloride thrown down with pure hydrochloric acid, and the precipitate washed first with dilute hydrochloric acid and then with pure water. The precipitate is next dried and the powder well rubbed up in a mortar. This is then repeatedly digested with aqua-regia and afterwards well washed, and the silver chloride reduced to metal by boiling with dilute chemically pure caustic potash to which milk sugar is added. The reduced silver is washed with dilute sulphuric acid and water dried and fused.

Pure silver is used in the laboratory for volumetric analysis. It is not necessary for this purpose to have it so pure as the metal employed by Stas for his atomic weight determinations, and it may be obtained sufficiently so by boiling well-washed silver chloride with caustic potash and sugar. The point of complete reduction is ascertained by taking a small portion out, washing it well with water, and dissolving in pure dilute nitric acid; if the reduction be complete it will dissolve without residue. The metal is then melted in a crucible together with some pure sodium carbonate or borax.

Molecular silver, employed in organic chemistry, is obtained according to Wislicenus, by bringing zinc into contact with finely-divided silver chloride which has been precipitated in the cold and washed until nearly free from acid. In a few hours the chloride is completely reduced and the precipitated silver may be separated from the sheet zinc by washing, and then treated with dilute hydrochloric acid to remove every trace of zinc. It is then brought on to paper and dried in the air and afterwards gently heated to 150°. Thus prepared it is a grey powder, possessing no metallic lustre, which, however, it assumes when rubbed under a burnisher or heated to redness.

168 *Properties.*—Silver possesses a pure white colour, and takes a high polish. Of all the metals it is the best conductor of heat and electricity, and is very tough and malleable, since 0·1 gram can be drawn out into a wire 180 m. in length and silver leaf can be beaten out to a thickness of 0·00025 mm. In the finely divided state, as obtained by the reduction of the chloride and other salts, silver presents the appearance of a dull dark grey powder.

Silver is precipitated in very thin films in the form of a lustrous metallic mirror-like deposit on glass from ammoniacal solution in presence of many reducing agents, especially organic substances; it then adheres to the glass and transmits blue light.

Metallic silver is found native in regular octohedra which frequently occur twinned, and also in dendritic forms. It is also often found in the crystalline form in silver melting furnaces.

Silver fuses at a temperature of 960·5° (Heycock and Neville). In the liquid state it possesses the power of absorbing oxygen from the air, which it gives up on solidification. When a mass of the metal is rapidly cooled the silver solidifies before the

oxygen has escaped from the interior; this gas then bursts through the crusts, and drives out part of the fused silver in globular masses and excrescences; this peculiar phenomenon is known as the "spitting" of silver. When charcoal powder is thrown on the surface of the metal the charcoal withdraws the absorbed oxygen, and consequently prevents silver from spitting. The same preventive effect is noticed when silver is fused under common salt, but when fused under nitre the spitting takes place. The presence of 5 per cent. of copper deprives silver of the power of absorbing oxygen.

Silver begins to volatilise at a white heat, and when heated in a lime-crucible by means of the oxyhydrogen blowpipe it may be readily made to boil. By this process Stas was able to distil fifty grams of pure silver in from ten to fifteen minutes; no residue whatever was left behind, and a portion of the vapour, which has a bright blue colour, was carried out by the current of oxygen gas, and rendered the air of the laboratory hazy, imparting to it a metallic taste. Distilled silver has a specific gravity of 10·575 (Christomanos); fused silver has a specific gravity of from 10·424 to 10·511 (Holzmann); whilst silver which has been exposed to pressure under the coining press has a specific gravity of 10·57 (G. Rose).

Pure silver is used in the laboratory in volumetric analysis and also in the preparation of chemical utensils, as this metal is not, like glass or platinum, attacked by fused caustic alkali.

Allotropic forms of silver.—By the action of different reducing agents such as sodium tartrate and citrate, ferrous sulphate, dextrin and tannin, on solutions of silver salts, Carey Lea has obtained a number of different precipitates which he regards as allotropic forms of silver. In 1889 he distinguished three different forms, viz. (1) a dull blue-black precipitate, which has a bluish-green metallic lustre when dry, and dissolves in water forming a deep red solution; (2) a dark reddish-brown precipitate; (3) a bronze-coloured precipitate which assumes the colour of burnished gold on drying. Subsequently he obtained a number of other modifications closely resembling the above, the latter being the most stable forms. The solutions obtained from them contain the silver in colloidal condition, and hence these substances are sometimes termed *colloidal silver*. Their conductivity is much less than that of ordinary silver, into which they readily pass when treated with many acids and salts, or when subjected to the action of heat or to friction. If the

gold-like modification be heated to a temperature just sufficient to carbonise paper, it yields a brighter yellow modification which is not so active and is unchanged by salts which act upon the other modifications. Carey Lea regards the first-named forms as consisting of silver in the atomic condition, whilst the less active yellow variety contains molecular silver, and the usual form of the polymerised silver.[1] Hitherto, however, these substances have not been prepared in the pure condition, usually containing up to 98 per cent. of silver, and until they have been obtained free from other compounds, the existence of allotropic forms of silver cannot be regarded as definitely proved.

Silvering and Plating.

169 Objects made of copper or of brass, bronze, German silver, or similar alloy are frequently silvered to give a bright and permanent surface to these metals. If the covering of silver be thick the goods are said to be plated; if thin, they are said to be silvered. Silvering may be effected either by a dry or by a wet process. Dry silvering is effected by rubbing silver amalgam on the surface of the metal, which has previously been cleaned by acids or by agitating the articles with this amalgam. On heating, the mercury is expelled and a very thin film of silver left behind, which, on burnishing, gives a bright silvery surface. Instead of the amalgam, a mixture of four parts of precipitated silver, sixteen parts of sal-ammoniac, sixteen parts of common salt, and one part of corrosive sublimate is employed, mixed together with water to form a paste.

Wet silvering is especially employed for the silvering of thermometer and barometer scales, divided circles, and the like. One process is simply to clean the surface of brass or copper by momentary immersion in nitric acid, and then, after washing it with water, to cover it with a mixture of equal parts of silver chloride and cream of tartar, or equal parts of chloride of silver, common salt, and whiting. The mixture is rubbed in until a sufficient deposit has been obtained. A second process is employed for silvering small

[1] *Amer. J. Sci.* 1889 (3), **37**, 476; **38**, 47, 129; *Phil. Mag.* 1891 (5), **31**, 238, 320, 497; **32**, 337; *Amer. J. Sci.* 1894 (3), **48**, 343; Schneider, *Ber.* 1891, **24**, 3370; 1892, **25**, 1164, 1281, 1440; Barns and Schneider, *Zeit. Phys. Chem.* 1891, **8**, 278; *Wied. Ann.* 1893, **48**, 357; Oberbeck, *Wied. Ann.* 1892, **46**, 265, 353, ; 1893, **48**, 745.

articles such as pins, buttons, &c.: for this purpose a solution of silver chloride in sodium sulphite or thiosulphate or in common salt, or cream of tartar, is employed; a warm solution is used, and the silver is instantly deposited upon the metallic object.

The *plating* of copper is effected by polishing the surface of the ingot which is to be plated, and then placing upon it a strip of bright silver, the area of which is somewhat smaller than that of the copper; the compound ingot is then exposed to a temperature slightly below the fusing point of silver, and by hammering or rolling at this temperature the two metals are sweated together, as it is termed; no soldering is employed in this process; the ingot is then rolled until it is reduced to the required thickness.

Electro-deposition of silver.—The process of electro-plating in silver was discovered by Messrs. Wright and Parkes of Birmingham in the year 1840. They were employed during that year in making experiments with a view of obtaining a bright and firm deposit of metallic silver by an electro-process similar to that by which Jacobi, Jordan, and Spencer had succeeded in obtaining the deposition of copper. Their attempts however were not completely successful, inasmuch as they either obtained only a very thin coherent film, or else the whole of the silver was thrown down in the form of a grey powder. At this juncture Mr. Wright met with a passage in Scheele's *Chemical Essays* (pp. 404–406), which soon proved of the highest importance to the commercial success of his undertaking, by enabling him to obtain suitable deposits of silver and gold. Speaking of the solubility of the oxides and cyanides of gold, silver, and copper, Scheele says that, "if these calces (that is the cyanides of gold and silver) have been precipitated, and a sufficient quantity of the precipitating liquor be added in order to redissolve them, the solution remains clear in the open air, and in this state the aërial acid (that is, the carbonic acid of the air) does not precipitate the metallic calx."[1] Working with this idea, Wright first employed a solution of chloride of silver in potassium ferrocyanide and quickly got a thick deposit of firm and white silver, a result which had never previously been obtained. Soon after that he found that the solution of silver cyanide in cyanide of potassium gave still better results; and, submitting his results to the well-known firm of G. R. and H. Elkington, a patent was taken out, and this patent process proved to be the foundation

[1] Gore, *Electro-Metallurgy*, p. 19.

of all electro-plating of gold and silver because it included the solutions of the alkaline cyanides, the only liquids which fulfil all the necessary conditions. The silver-plating solution consists of a solution of cyanide of silver in cyanide of potassium, an excess of the cyanide of potassium being added in order that no cyanide of silver shall separate out on the positive pole, which always consists of silver. The action which takes place in this electrolysis is the same as that described under copper electro-plating. The negative pole is connected with the object to be silvered, and upon this the silver is deposited, whilst at the positive pole cyanogen is formed; this combines with the silver which forms the pole, and the cyanide of silver thus formed dissolves in the excess of potassium cyanide.[1]

170 *Silvering of glass and mirrors.*—Many organic bodies possess the power of precipitating silver in the form of a highly coherent mirror when brought into contact with an alkaline silver solution; this mirror deposits in the form of a brilliant adhering mirror-like coating. Of the many methods which have been proposed for silvering on glass the first was one suggested by Liebig.[2]

In this process a *silvering liquid* (A) and a *reducing liquid* (B) are required.

In the preparation of the *silvering liquid* (A) the following solutions are employed:—

(1) A silver solution prepared by dissolving one part of fused nitrate of silver in ten parts of distilled water.

(2) An ammonia solution prepared either by neutralising pure nitric acid with ammonium carbonate and diluting it until the liquid has a specific gravity of 1·115, or by dissolving 242 grams of ammonium sulphate and diluting to 1200 cc.

(3) A soda solution prepared from materials free from chlorine and having a specific gravity of 1·050.

The silvering liquid (*A*) consists of 140 volumes of the silver solution, 100 volumes of the ammonia solution, and 750 of the soda solution. If ammonium sulphate be employed this must be poured into the silver solution, and then the caustic soda added in small portions at a time; the liquid is allowed to remain at rest until it becomes clear and then drawn off with a syphon.

The reducing liquid (*B*) is made as follows:—

(1) 50 grms. of white sugar candy are made into a thin syrup

[1] Further particulars respecting this interesting process can be obtained in Gore's *Electro-Metallurgy*.

[2] *Annalen Suppl.* 1867, **5**, 257.

with water, and boiled for an hour with 3·1 grms. of tartaric acid; this solution is then diluted with water to 500 cc.

(2) 2·857 grms. of dry tartrate of copper are moistened with water, and caustic soda solution is added drop by drop until the blue powder is completely dissolved, and the solution is then diluted to 500 cc.

The reducing solution (*B*) consists of one volume of the sugar solution, one volume of the copper solution, and eight volumes of water.

The glasses to be silvered are placed vertically one over the other; fifty parts of the silvering liquid (*A*), poured in and diluted with 250 to 300 volumes of water, and then ten parts of the reducing liquid (*B*) added. In winter warm water is employed, the temperature of the liquid being 20° to 28°. Optical glasses, especially specula of reflecting telescopes, silvered by this process, are largely employed. They must be placed in a horizontal position, so that they are only just covered by the liquid, and the surface of the silver must permit blue light to pass through it, be brightly lustrous, and so firmly attached that it is not removed by polishing. It is a singular fact that if too much copper be added no silver is deposited at all.

In another very good method of silvering glass, the following solutions are required :—

For the first solution 10 grms. of silver nitrate are dissolved in 80 cc. of water, and this poured into a rapidly boiling solution of 8 grms. of Rochelle salt in 3840 cc. of water, and the solution filtered on cooling. The second solution consists of 10 grms. of silver nitrate dissolved in 80 cc. of water; to this ammonia is added until the precipitated oxide is nearly re-dissolved, and the whole is diluted to 960 cc. The silvering liquid consists of equal volumes of the two solutions.

The following are the directions given by Browning for silvering glass specula.

Prepare three standard solutions :—

Solution A	Crystals of Nitrate of Silver	90 grains.
	Distilled Water	4 ounces.
Solution B	Potassa, *pure by Alcohol* . .	1 ounce.
	Distilled Water	25 ounces.
Solution C	Milk-Sugar (in powder) . .	½ ounce.
	Distilled Water	5 ounces.

Solutions A and B will keep, in stoppered bottles, for any length of time; solution C must be fresh.

"To prepare sufficient of the silvering fluid for silvering an 8-inch speculum proceed as follows:—Pour 2 ounces of Solution A into a glass vessel capable of holding 35 fluid ounces. Add drop by drop, stirring all the time (with a glass rod), as much liquid ammonia as is just necessary to obtain a clear solution of the grey precipitate first thrown down. Add four ounces of Solution B. The brown-black precipitate formed must be just re-dissolved by the addition of more ammonia, as before. Add distilled water until the bulk reaches 15 ounces, and add, drop by drop, some of solution A, until a grey precipitate, which does not re-dissolve after stirring for three minutes, is obtained, then add 15 ounces more of distilled water. Set this solution aside to settle. Do not filter. When all is ready for immersing the mirror, add to the Silvering Solution 2 ounces of Solution C, and stir gently and thoroughly."

In all processes of silvering glass it is absolutely necessary that the surface of the glass shall be completely clean, and in order that the silver coating may be permanent, it is usual either to varnish it or cover it with an electro-deposit of copper. This, however, must not be done in the case of glasses used for specula, as the reflecting surface must in this case be of silver.

ALLOYS OF SILVER.

171 The presence of small quantities of other metals, such as antimony, arsenic, bismuth, tin, or zinc, as also that of a small quantity of silver sulphide, renders silver brittle and liable to crack when rolled. The alloys of silver and copper are the only ones which are largely used in the arts. Almost all commercial silver is alloyed with copper, as pure silver is too soft for ordinary purposes such as coining and jewellery work. The addition of a small quantity of copper imparts to it a sufficient degree of hardness, and makes it tougher as well as more easily fusible. Thus for instance a wire of pure silver having an area of 1 sq. cm. breaks with a weight of about 2,800 kilos., whereas if it be alloyed with 25 per cent. of copper and drawn cold, it will sustain a weight of from 6,000 to 9,000 kilos.; after ignition it becomes soft, and breaks with a weight of from 3,800 to 4,800 kilos. It has been found that alloys of copper and silver, however perfectly the metals may be mixed and melted together,

undergo on solidification a process of liquation, the upper and the lower portions of the ingot differing in fineness from 0·002 to 0·015. As already stated (p. 67), Levol[1] has shown that the only alloy of these metals which does not exhibit this peculiarity is one having the specific gravity 9·9045, and the composition Ag_3Cu_2. If the fineness be less than corresponds to this formula, the superficial portion is richer in silver; when the percentage of silver is greater than this the interior portions are richest. The fineness of silver alloy is generally calculated upon a thousand parts; thus, for instance, the one above mentioned will have a fineness of 718. The colour of the silver-copper alloys becomes more and more red as the percentage of copper is increased, but an alloy of 1 part of silver and 4 of copper does not possess the true copper colour.

Silver Coin.—The proportion of copper in the standard silver used in different countries varies considerably. The English standard coinage silver contains 7·5 per cent. of copper, or has a fineness of 925; the specific gravity of the English silver is 10·30. In France three standard alloys are employed; one containing 950 per mille of silver for medals and plate; another containing 900 per mille for coin; and a third containing 800 per mille for jewellery work. In Germany and Austria the standard for coin contains 900 per mille of silver. The German alloy used for silver-plating contains from 700 to 810 per mille of silver.

The present composition of British silver coin is the same as that issued in the time of Edward I., the alloy in this reign containing 925 of fine silver, and being described as "the old standard of England."

Up to the year 1851 the manufacture of coin was intrusted to a private company termed the moneyers, who had to produce coin varying within very narrow limits, the alloy thus produced being compared with plates of standard silver termed "standard trial plates."

Since the above year the business of coining has devolved upon the Government, the Chancellor of the Exchequer being Master of the Mint. The ancient ceremony of the "trial of the pyx" is however still carried on every year. This consists in a public trial by competent assayers appointed by the freemen of the Goldsmiths' Company of the coin (both gold and silver) issued during the year. By this means the accuracy of the coin both as to fineness and as to weight is ascertained, and this trial

[1] *Ann. Chim. Phys.* 1849 [3], **26**, 220.

served in former days as the only safeguard against debasement of the coinage. The fineness of the coins is ascertained at the trial of the pyx by reference to the trial plates whose composition has been determined with the greatest accuracy.

The following table gives the accurate composition of trial plates of various dates, portions of which have been preserved and recently analysed [1] in the Royal Mint. The plates made in former times, when no accurate means of analysis existed, show considerable variation in the composition of the silver standard plates, the standard prescribed by law being in each case the same, viz., 925 :—

Date.	Fineness.
1477	923·5
1560	930·2
1660	924·2
1728	928·9
1829	925·0
1873	924·96

Silver is soldered by an alloy containing 6 parts of brass, 5 of silver, and 2 of zinc.

SILVER AND OXYGEN.

172 Silver forms two oxides :—

Silver oxide, Ag_2O.
Silver peroxide, AgO.

A third oxide known as silver suboxide was described by Wöhler,[2] who obtained it by acting on different silver salts with hydrogen, and by heating silver citrate in hydrogen, and treating the solution of the residue with caustic potash. Further investigations by Bailey and Fowler and by Muthmann have shown that such an oxide does not exist, the substance thus described being a mixture of silver and silver oxide. The peculiar red colour of the supposed solution of silver subcitrate is due to very finely-divided silver.

[1] W. C. Roberts, *Journ. Chem. Soc.* 1874, 197.
[2] *Annalen*, 1839, **30**, 1.

Silver oxide, Ag_2O.—This is the best defined oxide of silver, and is usually simply called oxide of silver or argentic oxide. It is obtained by precipitating silver nitrate with pure potash or soda. Thus prepared it forms a brown precipitate, which, when dried at a temperature of from 60 to 80°, becomes almost black. When freshly precipitated silver chloride is boiled with an excess of caustic potash, the same oxide is obtained in the form of a finely-divided bluish-black powder. It is soluble in about 3,000 parts of water, imparting to the solution a metallic taste and an alkaline reaction. In the moist condition it absorbs carbon dioxide from the air: it decomposes soluble chlorides with formation of silver chloride, and precipitates the corresponding oxide from solutions of many metallic salts. When heated to 250° it begins to decompose and loses the whole of its oxygen at 300°, whilst in the presence of hydrogen it is reduced to metal at 100°. When rubbed in a mortar with antimony sulphide, arsenic sulphide, milk of sulphur, amorphous phosphorus, tannic acid, or other easily oxidisable substances, ignition takes place. It is dissolved by ammonia, the solution on exposure to air yielding fulminating silver, a black explosive compound which has the composition NAg_3 (p. 376).

Silver oxide corresponds to the only well-defined series of silver salts, which may frequently be obtained from it by the action of the corresponding acid, but are usually formed by double decomposition, as most of them are insoluble in water, the principal exceptions being the nitrate and fluoride, which are readily soluble, and the sulphate and nitrite which are sparingly soluble. The salts with colourless acids are usually colourless, but a few, such as the bromide, iodide, phosphate and arsenate, are coloured. The soluble salts have a neutral reaction and unpleasant metallic taste and are poisonous. Many silver salts, such as the sulphate and thiosulphate, are isomorphous with the corresponding salts of sodium and lithium.

Silver Peroxide, AgO.—This substance discovered by Ritter in 1814, separates out on the positive pole, in the form of a black crystalline powder consisting of small octohedra, when a galvanic current is passed from platinum electrodes through a solution of 1 part of silver nitrate in 8 parts of water. It may also be obtained as an amorphous crust by using a silver plate as the positive pole, and allowing the current of electricity to pass through dilute sulphuric acid (Wöhler), and is likewise produced by the action of ozone on silver and silver oxide.

When heated it easily decomposes into oxygen and the metal, and is reduced by hydrogen at a low temperature with a slight explosion. If brought in contact with sulphur or phosphorus it deflagrates on being struck, and it dissolves in aqueous ammonia with evolution of nitrogen :—

$$6AgO + 2NH_3 = 3Ag_2O + 3H_2O + N_2.$$

It dissolves in concentrated sulphuric acid, imparting to the liquid a dark-green colour. The solution, which smells of ozone, is tolerably permanent, but when diluted with water oxygen is evolved and silver sulphate is formed ; with hydrochloric acid it yields silver chloride and chlorine :—

$$2AgO + 4HCl = 2AgCl + 2H_2O + Cl_2$$

It appears doubtful if this oxide has been obtained in the pure condition, and when prepared from silver nitrate it always contains the latter, double compounds having the composition $4AgO + AgNO_3 + H_2O$ and $10AgO + 2AgNO_3 + H_2O$ having been obtained. According to Berthelot the crystals obtained by the electrolysis of silver nitrate have the composition $4Ag_2O_3 + 2AgNO_3 + H_2O$, and the oxide Ag_4O_3 may be obtained by the action of hydrogen dioxide on moist silver oxide.[1]

Silver and the Halogens.

173 *Silver Subfluoride*, Ag_2F, is obtained as a bronze-like crystalline powder by heating a saturated solution of silver fluoride with metallic silver, and is re-converted into these by the addition of an excess of water.[2]

Silver Fluoride, AgF, is obtained by dissolving silver oxide or carbonate in aqueous hydrofluoric acid and evaporating to dryness. Hydrofluoric acid does not act upon metallic silver. If the solution be allowed to evaporate in a vacuum, colourless lustrous, deliquescent, quadratic pyramids are deposited, having the composition $AgF + H_2O$ (Marignac). The concentrated solution when allowed to stand exposed to the air, deposits hard transparent prisms of the compound $AgF + 2H_2O$, which are nearly as deliquescent as calcium chloride. It is extremely

[1] *Compt. Rend.* 1880, **90**, 572.
[2] Güntz, *Compt. Rend.* 1890, **110**, 1337.

difficult to obtain silver fluoride in the anhydrous state. The hydrate $AgF + H_2O$ decomposes when dried in a vacuum and yields a brown amorphous mass which still contains 1·5 per cent. of water, and dissolves in 0·85 parts of water at 15°·5. When heated to the melting point of lead in a covered crucible, 0·5 per cent. less than the calculated quantity of water is given off together with some hydrofluoric acid and oxygen:—

$$4AgF + 2H_2O = 4Ag + 4HF + O_2.$$

This decomposition goes on until all the water is driven off and the salt melted, and from this point it can be heated in absence of air up to the melting point of silver without any further decomposition taking place.[1] The fused salt solidifies to a black mass which is elastic and may be cut with scissors. In the fused state it conducts electricity without being decomposed. The dry pulverulent salt absorbs 844 times its volume of ammonia.

Silver Chloride, AgCl, occurs as the mineral *chlorargyrite* or *horn-silver*, which crystallises in octohedra and other forms of the regular system, but is more frequently found as a massive wax-like mass, which generally has a pearl-grey colour, though sometimes it possesses a whitish and sometimes a violet-blue colour. It occurs at Andreasberg, mixed with alumina, as an earthy mass which is called butter-milk ore, and this ore was known to the older mineralogists. Gesner, in 1565, terms horn-silver "Argentum cornu pellucido simile," and Matthesius, in his Berg-Postilla, published in 1585, terms it "glass-ore, transparent like horn in a lantern." The largest masses are brought from Peru, Chili, and Mexico, and the mineral also occurs in Cornwall, in Nevada, where it is abundant, in Arizona and other localities. The method of preparing silver chloride artificially was probably known to the old alchemists, but it is first distinctly mentioned in the works of "Basil Valentine," who says: "Common salt throws down ☽." This precipitate was afterwards termed *Lac argenti*, and when it was found that it was fusible, and solidified to a transparent horn-like mass, the name *Luna cornea*, first mentioned by Croll in 1608, was given to it. Libavius stated that the substance obtained by precipitating silver solution with common salt weighed less than the silver itself, but this statement was contradicted by

[1] Gore, *Phil. Trans.* 1871, 321.

Boyle; and Kunkel in his *Laboratorium Chymicum*, speaking of this, says that many substances are difficult to separate from one another: "Such is seen in ☽ cornea, as 12 loth ☽ retain out of the common salt, 4 loth terra and salt." This determination is in fact nearly correct, for 12 parts of silver form 15·94 parts of silver chloride.

Silver chloride is formed, without the phenomenon of incandescence, when chlorine is passed over silver at a dull red-heat (Stas). It is also formed by the action of hydrochloric acid on the ignited metal, whilst on the other hand hydrogen is able to reduce silver chloride to the metal (Boussingault). Aqueous hydrochloric acid converts the surface of metallic silver into chloride of silver, and common salt solution acts in a similar way. Proust examined some piasters which had for many years lain at the bottom of the sea, and he found that the whole of the silver was converted into chloride. In order to prepare pure chloride of silver a solution of the nitrate is precipitated by hydrochloric acid or common salt; in this way a white curdy precipitate is obtained which, on standing, or more quickly on agitation, becomes powdery. This precipitate must be washed and dried in absence of light. It has a specific gravity of 5·5. On heating, silver chloride assumes a yellow colour and melts at 450°, forming a dark yellow liquid. This solidifies on cooling, forming a botryoidal, colourless, tough, solid mass which refracts light strongly, and is so soft as to take impressions of the nail. It volatilises at a white heat, the vapour density agreeing approximately with the formula AgCl.[1]

According to Stas[2] fused chloride of silver is absolutely insoluble in water at the ordinary temperature, or at any rate its solubility does not reach the limit of our present tests for chlorine which Stas places at 1 in 10,000,000. In boiling water, on the other hand, it is slightly soluble. The precipitated curdy chloride is also slightly soluble in cold water; its solubility, however, is less when the precipitate has become powdery either by standing or shaking, 1 litre of water at 18° then dissolving 0·0017 gram. The solution becomes opalescent on the addition of either silver nitrate or hydrochloric acid. The presence of nitric acid does not affect the solubility of the curdy chloride, whereas the solubility of the powdery form increases proportionally to the amount of nitric acid added. One part of silver chloride dissolves in about 200 parts of concentrated

[1] *Zeit. Phys. Chem.* 1889, **4**, 267. [2] *Compt. Rend.* 1871, **73**, 998.

hydrochloric acid, and in 600 parts of the acid diluted with an equal bulk of water. Soluble chlorides, such as sal-ammoniac and common salt, dissolve silver chloride tolerably easily, and it is very soluble in ammonia, 12·88 parts of this substance of specific gravity 0·89 dissolving 1 part of the chloride of silver (Wallace and Lamont). When this ammoniacal solution is rapidly evaporated silver chloride crystallises out in glittering octohedra, but if the evaporation take place slowly crystals of $2AgCl+3NH_3$ are formed (p. 371). It is likewise dissolved in quantity by mercuric nitrate, sodium thiosulphate, and potassium cyanide. 100,000 parts of concentrated nitric acid dissolve 2 parts of the freshly prepared silver chloride (Thorpe); on boiling, it is decomposed into nitrate with evolution of chlorine.

Various metals, such as iron, zinc, &c., reduce the chloride to the state of metal in the presence of water, especially in presence of hydrochloric acid and sulphuric acid. It is also decomposed by mercury when a solution of common salt is present. Cold sulphuric acid does not act upon it, but it is decomposed slowly, though completely, by the boiling acid with evolution of hydrochloric acid.[1] Concentrated hydriodic acid decomposes it with evolution of heat into silver iodide (Deville), and if moist, freshly precipitated chloride be treated with a solution of bromide of potassium, or iodide of potassium, it is completely converted into silver bromide or iodide.[2]

White silver chloride, obtained by precipitation, when exposed to light is first coloured violet, then brownish-grey, and afterwards black. This alteration in colour was known to Boyle,[3] who, however, ascribed it to the action of the air. Scheele[4] afterwards proved that it was only discoloured on exposure to light, and he also showed that in this reaction hydrochloric acid was liberated, and that on treating the residue with ammonia, black flakes of silver remained behind.

It has been shown by Abney and by Baker that the pure chloride does not blacken when exposed to light in a vacuous tube, in perfectly dry oxygen or under pure carbon tetrachloride in the absence of oxygen. Baker[5] has also shown that not only is chlorine lost when the chloride blackens, but that oxygen is

[1] Sauer, *Zeit. Anal. Chem.* 1873, 376.
[2] Field, *Journ. Chem. Soc.* 1858, 234.
[3] *Op.* I. 756.
[4] *Von der Luft und dem Feuer*, Leipzic, 1784, p. 64.
[5] *Journ. Chem. Soc.* 1892, i. 728.

at the same time absorbed, an oxychloride of silver, Ag_2ClO, being probably formed. The amount of silver chloride which undergoes this change is, however, extremely small, even when a large quantity is exposed for a long period. The blackening is accelerated by the presence of substances which are capable of taking up chlorine, such as water, silver nitrate, stannous chloride, &c., and retarded by such as readily give up chlorine, such as chlorine water, ferric chloride, &c. Some chemists still support the view that a sub-chloride of silver is produced.

Silver Chloride and Ammonia, $2AgCl + 3NH_3$.—Glauber states that a calx is formed when silver solution is precipitated by common salt, and he adds that the calx "readily dissolves in *spiritu urinæ, salis armoniaci, cornu Cervi, succini, fuliginis et capillorum*, and may be used to form a good medicament." Faraday[1] first obtained this substance by the direct union of ammonia and silver chloride by saturating dry precipitated silver chloride with ammonia; 100 grains or 6·48 grams absorbed 130 cubic inches or 2·13 liters of the gas. According to Rose,[2] the increase of weight amounts to from 17·31 to 17·91 per cent., corresponding to the above formula. The absorbed ammonia is again given off at 37°·7 (Faraday). When heated in a closed tube for the purpose of obtaining liquid ammonia, the compound fuses between 88° and 95°, swells up, and begins to boil at 99°, losing ammonia and gradually becoming white. When a solution of silver chloride in concentrated ammonia is allowed to stand in an imperfectly closed bottle, large transparent rhombohedra are obtained which blacken on exposure to light, and when acted on by air or water, give off their ammonia, being converted into white friable chloride of silver (Faraday).

Silver Bromide, AgBr, occurs in Chili and Mexico as the mineral bromargyrite, being usually found in small yellow or greenish masses, rarely crystalline. The mineral embolite is a mixture of silver chloride and bromide, varying from three of the latter to one of the former to the reverse proportion. It likewise occurs in Chili and Mexico, and is very similar to the foregoing mineral. When an excess of silver nitrate is precipitated in the dark with hydrobromic acid, a white curdy precipitate is obtained which in contact with potassium bromide, or on heating, becomes yellow. It is soluble in a hot solution

[1] *Quart. Journ. of Science*, 1818, **5**, 74.
[2] *Pogg. Ann.* 1830, **20**, 157

of hydrobromic acid, and in a solution of mercuric nitrate, separating out in octohedra from these solutions on cooling. It is scarcely soluble in dilute ammonia, but easily soluble in concentrated ammonia, and melts, on heating, to form a reddish liquid which solidifies to a yellow lustrous mass, and the latter, when heated in a current of chlorine, is slowly converted into chloride. The finely divided precipitate suspended in water is instantly decomposed by chlorine, and hydrochloric acid gas also decomposes it at 700° with evolution of hydrobromic acid. Whilst the fused bromide is hardly acted upon by light, the precipitated salt is soon coloured a greyish-violet on exposure to light; if, however, it contains a trace of free bromine, it is unacted on. The action is also lessened by the presence of nitric acid, whilst it is increased by the presence of silver nitrate. Stas[1] describes several varieties of this salt which differ in their behaviour towards light. Dry silver bromide absorbs no ammonia;[2] on the other hand, the ammoniacal solution deposits on standing white glistening crystals, and these on heating lose ammonia.[3]

Silver Iodide, AgI.—This salt occurs as iodargyrite, in Mexico, Chili, Spain, and in the Cerro Colorado Mine in Arizona, in the form of slightly elastic hexagonal tables. Silver combines directly with iodine on heating. The metal also dissolves in hydriodic acid, with violent evolution of hydrogen, and if the liquid be warmed as soon as the action becomes lessened the evolution again increases, and on cooling colourless crystalline scales separate out. These on exposure to air decompose quickly, and probably possess the formula AgI,HI. The mother-liquid on standing, deposits thick hexagonal prisms of silver iodide.[4] The same compound is formed by the action of concentrated hydriodic acid on silver chloride. It is also formed by the treatment of the chloride or bromide of silver with aqueous potassium iodide or other soluble iodides, silver iodide being deposited as a light yellowish powder. It melts at 550° forming a yellow liquid, which on further heating becomes red and then dark reddish-brown, and on cooling solidifies to a yellow soft mass having a specific gravity of 5·687 at 0° (Deville), whilst the crystalline variety has at 14° a specific gravity of 5·669,

[1] *Ann. Chim. Phys.* 1874 (5), **3**, 289.
[2] Rammelsberg, *Pogg. Ann.* 1842, **55**, 246.
[3] Liebig, *Schweig. Journ.* **48**, 103.
[4] H. Deville, *Compt. Rend.* 1851, **32**, 894.

that of the precipitated salt being 5·596 (Damour). An interesting fact with reference to the abnormal expansion and contraction of silver iodide by heat has been observed by Fizeau;[1] it contracts when heated from − 10° to + 70°, and expands on cooling. This is explained by Rodwell,[2] by the fact that silver iodide exists in two modifications.

Pure silver iodide is left unaltered by the action of direct sunlight. If, however, it be precipitated from an excess of silver nitrate so that traces of this salt are carried down with it it becomes coloured green on exposure to light, and in presence of more silver nitrate, a deep greyish-black colour is attained although no loss of iodine is observed (Stas). Iodide of potassium and nitric acid having a specific gravity of 1·2 have the power of reproducing the yellow colour. The changes effected by light upon silver iodide are brought about chiefly in the presence of substances which have the power of combining with a portion of the iodine. Ammonia changes the yellow colour of silver iodide to white and dissolves it very sparingly; it differs from the chloride and bromide of silver, inasmuch as it is difficultly soluble even in concentrated ammonia, one part of the iodide dissolving, according to Wallace and Lamont, in 2493 parts of ammonia of specific gravity 0·89. It is tolerably soluble in a strong solution of potassium iodide, from which solution it is precipitated on the addition of water. A hot solution of potassium iodide saturated with silver iodide, deposits on standing white needles of a salt having the composition AgI,KI. When silver iodide is gently heated in chlorine gas, it decomposes into silver chloride and the same reaction takes place when it is treated with dry hydrochloric acid at 700° (Hautfeuille). It is only incompletely reduced in a current of hydrogen even when exposed to a white-heat (Vogel). The dry precipitated iodide absorbs 3·6 per cent. of ammonia gas forming a white compound, $2AgI,NH_3$, which on exposure to air gives off ammonia and turns yellow again.[3]

Silver Chlorite, $AgClO_2$, is obtained by precipitating a weak alkaline solution of a chlorite with silver nitrate. It forms a crystalline powder which separates from a solution in hot water in crystalline scales. These deflagrate when moistened with concentrated hydrochloric acid or when heated to 105°; they also take fire when mixed with sulphur (Millon).

[1] *Compt. Rend.* 1867, **64**, 304. [2] *Chem. News*, 1875, **31**, 4.
[3] Rammelsberg, *Pogg. Ann.* 1839, **48**, 170.

Silver Chlorate, $AgClO_3$.—This salt is obtained when chlorine is passed into water through which silver oxide is diffused, until bubbles of oxygen are evolved; the chloride of silver is filtered off and the liquor evaporated to its crystallising point. The filtrate first contains silver hypochlorite, which however decomposes in the dark at 60° as follows:

$$3AgClO = 2AgCl + AgClO_3.$$

The chlorate may also be obtained by dissolving silver oxide in chloric acid, the action being accompanied with evolution of heat. It crystallises in white opaque quadratic prisms, having a specific gravity of 4·43. These dissolve in about 10 parts of cold water and melt at 230°; when further heated to 270° they give off oxygen and a trace of chlorine. When mixed with sulphur it detonates with the utmost violence on friction.

Silver and Sulphur.

174 *Silver Sulphide*, Ag_2S, occurs as argentite, or vitreous silver. The occurrence of this ore was known to Agricola: "Argentum rude plumbei coloris et galenæ simile." This important silver ore, occurring in blackish-grey crystals, belonging to the regular system, occurs widely distributed, but is found especially in the Erzgebirge, in Hungary, in Norway near Kongsberg, in the Altai, in the Urals, in Cornwall, Bolivia, Peru, Chili, Mexico, and in Nevada, at the Comstock lode. This compound occurs in the Erzgebirge, in two distinct forms; one of these is termed daleminzite, and the other acanthite; the first of these being isomorphous with chalcocite. Argentite can be obtained artificially, by igniting silver chloride in a current of sulphuretted hydrogen. Silver sulphide is also formed when silver is heated with sulphur or sulphuretted hydrogen, and forms the yellow or brownish stains which are formed on articles of silver on exposure to the air (Proust). Sulphuretted hydrogen produces in solutions of silver a blackish-brown flocculent precipitate of silver sulphide which is soluble in hot nitric acid, and is converted into silver chloride when a solution of copper chloride in the presence of common salt is added to it.

Silver Sulphite, Ag_2SO_3, is a white curdy precipitate almost insoluble in water and sulphurous acid, decomposing when heated to 100° into silver and silver sulphate.

Normal Silver Sulphate, Ag_2SO_4.—This substance was obtained in solution by Glauber, for he states in his *De furnis novis philosophicis* (1648), "Dissolve *rasuram* ☽ in a rectified oil of vitriol, with the addition of a sufficiency of water, but not so much as in the case of Mars or Venus. Or, still better, dissolve a calx of ☽ which is precipitated from aqua fortis, either by copper or by spirits of salt."

It is best obtained by heating the reduced metal with sulphuric acid, or by dissolving the carbonate in dilute sulphuric acid. It forms small lustrous rhombic crystals, which are anhydrous and isomorphous with anhydrous sodium sulphate;[1] it has a specific gravity of 5·4 and dissolves in about 200 parts of cold and 68·35 parts of boiling water. In consequence of the slight solubility of the salt, it is obtained as a precipitate when sulphuric acid or a soluble sulphate is added to a silver solution, and this fact was known to Boyle.[2] It is easily soluble in water containing sulphuric acid, and still more soluble in nitric acid and also dissolves readily in strong sulphuric acid, being precipitated from this solution on the addition of water. It fuses at a dark red-heat and decomposes at a very high temperature into metal, oxygen, and sulphur dioxide. When dissolved in less than three parts of sulphuric acid, light yellow prisms of hydrogen silver sulphate, $HAgSO_4$, are obtained.

According to Carey Lea[3] a double salt of silver sulphate and a lower sulphate, having the formula $Ag_4SO_4 + Ag_2SO_4 + H_2O$, is obtained by the reduction of silver nitrate, phosphate or carbonate with hypophosphorous acid in presence of sulphuric acid; it forms a pale brown powder which is permanent in the air and does not evolve sulphuric acid even at a dull red-heat. It always contains about 2 per cent. of phosphoric anhydride, which cannot be removed even by treatment with strong sulphuric acid.

Silver Thiosulphate, $Ag_2S_2O_3$, is obtained by gradually adding a moderately dilute solution of silver nitrate to an excess of concentrated solution of sodium thiosulphate, washing the precipitated grey mixture of thiosulphate and sulphide with cold water, extracting the thiosulphate with ammonia, precipitating it as quickly as possible by exact neutralisation with nitric acid and quickly drying it by pressure between filter

[1] Mitscherlich, *Pogg. Ann.* 1827, **12**, 138.

[2] "Considerations and Experiments touching the origin of qualities and forms," Boyle, *Op.* **3**, 66.

[3] *Amer. J. Sci.* 1892 (3), **44**, 322.

paper.[1] It forms a snow-white powder, having a sweet taste, and is slightly soluble in water, and in the moist condition it easily decomposes into sulphuric acid and sulphide of silver (Rose):

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

Silver Sodium Thiosulphate, $AgNaS_2O_3$, was discovered by Herschel, and may be obtained by evaporating a solution of silver chloride in aqueous sodium thiosulphate, until it crystallises. It is, however, best formed by adding a neutral solution of silver nitrate to a solution of sodium thiosulphate, until a permanent precipitate is produced. The solution is then filtered and alcohol added, when the salt is precipitated in silky laminæ (Lenz). Its solution, evaporated in a vacuum, deposits tabular crystals of the salt. It is soluble in water and possesses a sweet taste (Herschel).

Silver and the Elements of the Nitrogen Group.

175 *Silver Nitride,* NAg_3.—This compound, usually known as Berthollet's fulminating silver, was first obtained by the above-named chemist in 1788, by the action of ammonia on the silver oxide prepared by precipitating a silver solution with lime-water. It is a black powder which, especially in the dry state, explodes most violently on the slightest percussion or even on touching with a feather. Raschig[2] has shown that the compound has the composition NAg_3, but it is usually mixed with a certain quantity of metallic silver. In some cases the powder was also found to contain hydrogen and had then the formula $NHAg_2$.

Silver Azoimide, N_3Ag, is obtained by the addition of silver nitrate to a solution of azoimide or one of its soluble salts. It forms minute prisms which are insoluble in water, and readily explode with extreme violence.

Silver Hyponitrite, $Ag_2N_2O_2$ is a yellow precipitate which is stable at 100° but explodes violently when heated to 150°.

Silver Nitrite, $AgNO_2$.—This substance was first obtained by Proust, who regarded it as the nitrate of silver suboxide, having obtained it by boiling a solution of silver nitrate with the powdered metal. It is best prepared by mixing lukewarm solutions of 24 parts of silver nitrate and 15 parts of potassium

[1] Herschel, *Edin. Phil. Journ.* **1**, 26; **2**, 154. [2] *Annalen*, 1886, **233**, 93.

nitrite. On cooling, silver nitrite separates as a white crystalline powder, which may be readily filtered. It is less soluble in cold water than silver sulphate, but dissolves more readily in hot water with partial decomposition. When slowly deposited it forms long acicular rhombic crystals.

Silver Nitrate, $AgNO_3$.—This salt was obtained in the crystalline form by Geber: "Dissolve ☽ calcinatam in aqua dissolutiva, quo facto, eoque eam in phyala, cum longe collo, non obturato ori per diem solum, usque quo consumetur ad ejus tertiam partem aquæ, quo peracto pone in loco frigido, et devenient lapilli ad modum crystalli fusibiles." At the end of the seventeenth century, Angelus Sala drew the attention of the iatro-chemists to this salt known as *crystalli dianæ* or *magisterium argenti*, to which when cast into sticks, the name of *lapis infernalis* or *lunar caustic* was given.

Silver nitrate is obtained on the large scale, by dissolving silver in dilute nitric acid, and occurs in commerce both in crystals and cast into sticks (lunar caustic). It crystallises in transparent rhombic plates (Fig. 87), having a specific gravity of 4·328 (Schröder) and melting at 198°, solidifying on cooling to a white fibrous crystalline mass. It possesses an acrid metallic taste, and acts as a violent poison, blackening and destroying organic matter, but it does not blacken in the air except in contact with organic substances. When it is wrapped up in paper for some time it gradually decomposes, leaving a residue of metallic silver, and at a red-heat it yields nitrogen peroxide, oxygen, nitrogen, and metallic silver. According to Kremers,[1] 100 parts of water dissolve as follows:

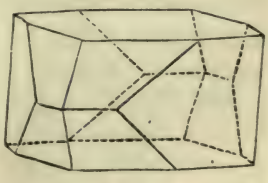


Fig. 87.

At	0°	19°·5	54°	85°	100°
$AgNO_3$	121·9	227·3	500	714	1,111 parts.

The aqueous solution has a neutral reaction. If ammonia be added to a solution of silver nitrate until the precipitate first formed redissolves, and this solution be then allowed to evaporate, fine bright rhombic prismatic crystals, having the composition $AgNO_3 + 2NH_3$, are deposited. These do not give off

[1] *Pogg. Ann.* 1854, **92**, 497.

ammonia at 100°, but when more strongly heated they melt, evolving nitrogen and ammonia, whilst ammonium nitrate and a metallic mirror of silver are left behind. When a current of dry ammonia is passed over dry silver nitrate, this substance absorbs 29·55 per cent. of the gas, enough heat being developed to produce fusion of the mass. The product of this reaction is a white solid soluble in water and possessing the formula $AgNO_3+3NH_3$ (Rose).

Silver nitrate is largely used in chemical analysis and especially in photography. It is also employed in medicine, both externally and internally. For external application it acts as a powerful cautery, inasmuch as it unites with the albuminoid substances to form insoluble compounds. Large doses given internally, act corrosively upon the mucous membrane, producing serious inflammation. Experiments on animals have shown that it produces paralysis of the nerve centres, difficulty of breathing, and coma. It is given in doses of from 0·02 grams in chronic stomach diseases, epilepsy and other nervous affections. When administered for some length of time, it produces a peculiar bronze colour of the skin, caused by the deposition of metallic silver under the cuticle.

176 *Phosphates of Silver.*—The normal phosphate, Ag_3PO_4, is formed as a yellow precipitate, when a silver salt is added to a solution of any one of the sodium ortho-phosphates. On heating, its colour changes to brown, and it melts at a red heat. It is soluble in aqueous phosphoric acid, yielding the mono-hydrogen salt, HAg_2PO_4, which is deposited in the form of white crystals. The pyrophosphate, $Ag_4P_2O_7$, is a white precipitate, melting below a red-heat, to form a dark-brown liquid which solidifies to a colourless fibrous mass. When heated for some time with aqueous phosphoric acid, the dihydrogen pyrophosphate, $H_2Ag_2P_2O_7$, is formed as a crystalline powder, which is decomposed on the addition of water. The metaphosphates of silver are white precipitates.

Arsenites and Arsenates of Silver.—The normal arsenite Ag_3AsO_3, is a canary-yellow powder, easily soluble in nitric acid and ammonia. When the ammoniacal solution is boiled, metallic silver separates out. The normal arsenate, Ag_3AsO_4, is a dark red-brown crystalline powder, formed by precipitating a concentrated solution of arsenic acid with a boiling solution of silver nitrate. The same substance is precipitated as a brownish-red powder, if a solution of an arsenate be added to silver nitrate.

Silver Carbonate, Ag_2CO_3, is a light yellow powder of a paler colour than the phosphate, which readily becomes black on exposure to light, or on heating, and loses all its carbon dioxide at 200°. When a mixture of ammonio-nitrate of silver and caustic potash is exposed to the air, silver oxide separates out, and after a time lemon-yellow needles of the carbonate.

Silver Cyanide, AgCN, is a white curdy precipitate, insoluble in dilute nitric acid but easily soluble in ammonia. It forms soluble double salts with the cyanides of the metals of the alkalis, and alkaline earths.

Potassium Silver Cyanide, $KAg(CN)_2$, crystallises in feathery tufts or six-sided prisms, and is soluble in 4 parts of water at 20°.[1] It does not undergo alteration on exposure to light.

Silver Cyanate, AgOCN, is a white precipitate easily soluble in ammonia and nitric acid. On heating it explodes, a dull white mass of silver carbide remaining behind. This decomposes, on solution in nitric acid, leaving a finely divided network of pure carbon.[2]

Silver Thiocyanate, AgSCN, is a white curdy precipitate, easily soluble in ammonia, crystallising from the solution in glistening scales, which do not contain any ammonia.

Potassium Silver Thiocyanate, $KAg(SCN)_2$, is formed when the foregoing salt is dissolved in a solution of potassium cyanide. It forms monosymmetric crystals, melts at 140°, and is decomposed by water.

Photography.

177 The observation of Boyle, that silver chloride and other silver salts undergo blackening on exposure to light, the chemical explanation of which was first given by Scheele, has led to the foundation of the important art of photography. The first light-pictures were obtained by Thomas Wedgwood, in the year 1802, These were simply prints of leaves or paintings on glass. prepared by allowing the light to fall through a more or less transparent object on to white paper, or leather, which had been moistened with nitrate of silver. Davy, repeating these experiments, obtained fairly accurate copies of leaves, wings of insects, and similar objects, and even succeeded in preparing pictures of small objects which had been magnified by the solar

[1] Baup, *Ann. Chim. Phys.* 1858, [3], **53**, 462.
[2] Liebig and Redtenbacher, *Annalen*, 1841, **38**, 129.

microscope. The pictures thus obtained could not be exposed to day-light, but had to be examined by candle-light, as at that time no process was known by which that portion of the silver salt unacted upon by the light could be withdrawn, and the picture thus rendered permanent. The first experiments which aimed at rendering the photographic image permanent were made by Niépce, who began his investigations in the year 1814. In 1826 he, together with Daguerre, investigated the same subject, and it is to the latter experimenter that we are indebted for the first process by which the image obtained in the camera can be fixed. In 1839 he discovered the process which now bears his name. This consists in allowing the vapour of iodine to act upon a polished surface of silver, which thus becomes coated with a film of silver iodide. The surface of the plate thus prepared is next exposed to light in the camera. After a short time the light has produced its action, although on the removal of the plate no change of the surface is perceptible. If the plate be now exposed to the action of the vapour of mercury, the picture makes its appearance, inasmuch as the mercury is deposited in extremely fine globules on those portions of the plate on which the light has fallen, whilst in the shadows, the unaltered iodide remains. The plate must next be dipped into a solution of sodium thiosulphate, in order to remove those portions of the iodide which have been unacted upon by the light.

The Daguerreotype process underwent many alterations, but it has now been altogether superseded by much more convenient methods. In the year 1839, Fox Talbot published his method of photogenic drawing, or photography, on paper. This process, which was but an imperfect one, consisted in exposing in the camera a paper soaked in a weak solution of common salt and afterwards washed over with a solution of silver nitrate. The image obtained was a negative one; that is, the light portions of the landscape were dark, and *vice versa*. These pictures were fixed by immersion in a solution of common salt. A great improvement was made in this process by Talbot, in the year 1841, by coating the paper which was to be acted upon with a film of silver iodide by first dipping it into nitrate of silver solution and then into one of potassium iodide. This paper does not exhibit any change after exposure in the camera, but on "development" with a mixture of silver nitrate, acetic acid and gallic acid, the image becomes visible. The picture is

a negative, but it may be rendered transparent by saturating it with white wax, and then a positive print may be prepared from it by placing it on a paper moistened with chloride of silver, and exposing it to sunlight. This method was long known as the Talbotype or Calotype process.

A most important improvement in photography was made by Archer (1851), in the employment of a transparent film of iodised collodion spread upon glass as a sensitive film for the camera in place of the iodised paper used in the Talbotype process. Collodion is a solution of pyroxylin, consisting of the lower nitrates of cellulose in a mixture of alcohol and ether, and to this is added a certain proportion of soluble iodide or bromide, usually of zinc or cadmium. · On pouring this solution on to the plate the ether and alcohol evaporate, and the plate becomes covered with a homogeneous film. The collodionised plate is next dipped into a bath of nitrate of silver, and the plate thus "sensitised" is exposed, still wet with the silver nitrate solution, in the camera. The image produced on the film is, in this case also, latent, and requires to be developed, or made visible, by treating the surface with reducing agents, such as ferrous sulphate or pyrogallic acid, compounds which have the power of reducing it to the condition of metallic silver. The unaltered iodide may be removed by dissolving it in cyanide of potassium or sodium thiosulphate, and from the negative thus obtained any number of positive prints can be prepared, each of which is afterwards fixed in sodium thiosulphate. The application of collodion renders the process much more certain, shortens the necessary exposure to a few seconds, and admits of a far greater degree of precision in the reproduction of detail than was possible on the rougher surface of paper in the Talbotype.

Many attempts were made to lessen the inconvenience attaching to wet plate photography by washing the plate free from silver nitrate and then covering it with a film of some substance such as tannin, albumen, &c., and then drying.

All these plates are, however, much surpassed in sensitiveness towards light by the modern dry plate, which consists of a glass plate coated with an emulsion of silver bromide, sometimes accompanied by a little iodide, in gelatin. This emulsion is made by adding an excess of potassium bromide to a solution of silver nitrate and gelatin in hot water. The mixture is then heated at 100° for some time, a process termed "ripening," until the emulsion attains its most sensitive condition. During

this operation a physical change appears to occur, the particles of bromide, which when first precipitated have a diameter of 0·0008–0·0015 mm., increasing during the process to 0·003–0·004 mm. in diameter. The emulsion is then washed, to remove the potassium bromide and nitrate, placed on the plate in a uniform film and dried. When such a plate is exposed to light a latent image is produced which can be developed by many reducing agents which do not attack unexposed silver bromide. If an exposed plate be treated with a halogen element or an oxidising agent such as nitric acid, potassium bichromate, &c., it is found that the image can no longer be developed. The reducing agents usually employed as developers are ferrous oxalate, which passes during the process into ferric oxalate, pyrogallic acid (tri-hydroxybenzene) or hydroquinone (quinol, paradihydroxybenzene) in presence of ammonia and ammonium bromide, which are converted by oxidation into quinones, and similar substances.

The exact change which is effected by the light is not yet completely understood. According to the view held until quite recently a very small amount of chemical change occurs during exposure, bromine being lost by the silver bromide and taken up by the gelatin, which thus acts as a sensitiser and replaces the silver nitrate of the wet collodion plate and the tannin of the dry collodion plate. During development the altered silver bromide is first developed and the reducing action becomes extended to the silver bromide in the immediate proximity of this reduced silver. It will be seen that according to this view the density of the silver image which can be obtained by development is only limited by the thickness of the film, the amount of silver produced increasing steadily with the duration of the development. It has, however, been shown by Hurter and Driffield [1] that the maximum density attainable depends entirely on the length of the exposure and the intensity of the light and is not altered by prolonging the development beyond a certain necessary time. The same chemists have further proved that when a plate is exposed so long that the whole of its silver bromide can be reduced to metallic silver by development, no evidence of the formation of hydrobromic acid, which would accompany the action of bromine on gelatin, can be detected, and that the whole of the bromine in the plate is given up to the developing liquid. This result therefore makes

[1] *Journ. Soc. Chem. Ind.* 1890, 455.

it appear probable that no actual chemical decomposition is effected by the light, but only some physical alteration which renders the silver bromide capable of undergoing reduction more easily. It is not impossible that the invisible change thus produced on the film may resemble that observed when light is allowed to fall on a mixture of chlorine and hydrogen. For these gases, which combine on insolation, require to be exposed to light for a certain length of time before any combination whatever takes place, this peculiar phenomenon being termed photo-chemical induction (Bunsen and Roscoe). In the case of the photographic image, the film undergoes a modification such as to render it susceptible to decomposition in presence of a reducing agent.

The question cannot however as yet be considered as settled.

178 *Action of Light of Different Degrees of Refrangibility on the Salts of Silver.*—Scheele observed that the violet rays of the solar spectrum are those which affect silver chloride most strongly, and to these the name of the chemical rays has frequently been given. It has, however, been shown that all the rays of the solar spectrum are able, under certain circumstances, to effect chemical change, each particular chemical compound being decomposed by the rays upon which it is most capable of exerting an absorbent action. Not only is this the case, but an admixture with the sensitive compound of certain coloured, but chemically inactive, substances has the effect of altogether altering the position of the maximum of chemical action for that particular substance. Thus, for example, it is possible by the addition of a yellowish-red colouring matter, such as aurin, to the bromide-film to prepare a plate which is affected as much by the yellow rays, which are usually considered chemically inactive, as by those in the violet. In this way Draper,[1] Vogel,[2] and Abney,[3] have succeeded in photographing the lines of the visible solar spectrum from *b* downwards, and have not only secured pictures of the portions included between the lines *E* and *A*, but have obtained photographic action even in the ultra-red regions. Orthochromatic plates are now made by means of which the relative intensity of the various colours to the eye is much more truly represented. The exact function of the dyes in producing this effect is not understood.[4]

[1] *Phil. Mag.* 1877, [5], **3**, 86. [2] *Pogg. Ann.* 1877.
[3] *Phil. Mag.* 1878, [5], **5**, 61. [4] *See* Bothamley, *Brit. Ass. Rep.* 1895, 661.

For a full account of the theory and practice of photography, the reader is referred to Abney's Treatise on Photography, and to Meldola's "Chemistry of Photography."

Detection and Estimation of Silver.

179 There is probably no element whose presence can be more readily detected by chemical methods than silver, owing to its chloride being insoluble in water and easily soluble in ammonia. In order to detect silver in an insoluble compound, it may be melted with sodium carbonate on charcoal before the blow-pipe or heated on the end of a carbonised lucifer-match in the reducing flame of the Bunsen burner. Silver is then obtained in the metallic state as a bright shining bead, which easily dissolves in warm nitric acid, the solution giving on the addition of hydrochloric acid a curdy precipitate of silver chloride, or, if only a trace of silver be present, a mere opalescence. This disappears on the addition of ammonia, but is reproduced when the ammonia is neutralised with nitric acid.

The spark spectrum of silver is obtained by the use of the metal as poles with a powerful discharge. It may also be seen when platinum poles are moistened with nitrate of silver solution. Two bright green lines are the most characteristic in its spectrum, and several weaker lines occur in both the blue and the violet.

Silver is almost always estimated quantitatively as the chloride. The precipitate after washing and drying is heated in a porcelain crucible until it begins to melt and then its weight is obtained. In order to determine the small quantity of chloride which adheres to the filter, the whole is burnt, the chloride being reduced to metallic silver. The weight of metallic silver and ash is thus obtained, and by subtracting the weight of the latter we get the weight of metallic silver present; the equivalent quantity of chloride is then calculated, and the number thus obtained added to the weight of the chloride already found.

In some few cases the silver is determined as the cyanide or sulphide, and, in the case of organic silver salts, the metal which remains behind on heating the salt is weighed.

Silver can also be easily determined volumetrically with

standard hydrochloric acid, common salt solution, or potassium thiocyanate. In the mints, where a large number of silver assays has to be made daily, a method proposed by Gay Lussac[1] is now almost universally adopted. In this process the alloy is dissolved in nitric acid, and the silver precipitated from solution in the form of chloride, the volume of the standard solution necessary for the complete precipitation of the silver being ascertained. Chemically pure silver is required for this purpose; this is best used in the form of thin foil; then a standard solution of common salt is needed of such a strength that 100 c.c. correspond exactly to one gram of silver; thirdly a salt solution 1-10th of this strength, prepared by diluting one volume of the standard solution with nine volumes of water, and lastly, a silver solution of exactly equivalent strength obtained by dissolving one gram of silver in pure nitric acid and diluting this to one liter. All these solutions must be made with care, and their strength very accurately ascertained.

The metal is dissolved in nitric acid, and the standard solution of common salt added gradually, the bottle being well shaken after each addition in order that the silver chloride may separate in a coherent form. As soon as the point of complete precipitation is seen to be approaching the standard solution of salt is replaced by the one of 1-10th strength which is added drop by drop until the precipitation is complete. Each c.c. of standard solution corresponds to 0·01 gram, and each c.c. of the second solution to 0·001 gram of silver.

Another method of assaying silver still used, although not so accurate as the method just described, is the assaying of silver by cupellation. Every silver article made in this country, previously to being sold, is tested at Goldsmiths' Hall by this method, and, if approved, is stamped. This process depends on the fact that the metals alloyed with silver oxidise in the presence of lead oxide at a high temperature, yielding a fusible glass which, together with the oxide of lead, is easily absorbed by the porous cupel, whilst any silver which the mixture contains is left behind in a bright globule which can be accurately weighed. The assay is usually made with one gram of silver. The process of assaying by cupellation, even in experienced hands, may

[1] *Instruct. sur l'Essai des Matières d'Argent par la Voie Humide.* Paris, 1833.

vary as much as two parts in 1,000, whilst Gay Lussac's process admits of an accuracy of 0·5 in 1,000. The process of cupellation is, however, still in use in lead works, where it is required to determine the amount of silver which marketable lead contains, and it is also used for the estimation of silver in poor ores.

The atomic weight of silver was determined with extreme accuracy by Stas, by the methods described on p. 12, the average of the numbers obtained by the different methods being 107·13 (O = 15·88).

GOLD (AURUM), Au = 195·7.

180 Of all the metals gold was probably the first to attract the attention of man, its occurrence in the native state, its brilliant lustre and its permanence rendering it an object of value from very early times.

Metallic gold is mentioned in the Old Testament and in Homer, and the various names by which it is designated denote lustre or fine colour. Thus in the Hebrew *zaháb*, the root signifies to glitter; whilst the Greek word χρυσός, probably derived from the Sanscrit *hiranya*, also signifies to glitter or flame. Our word "gold" probably is connected with *jvalita*, which also occurs in Sanscrit and is derived from *jval*, which also means to shine. As being the most perfect of the metals gold was compared by the alchemists to the sun; to it was attributed the most singular virtues, and strenuous efforts were directed to the transmutation of the baser metals into ☉ (Sol)[1]

Gold is usually found in the native state, but never perfectly pure, being always alloyed with more or less silver. If it contain more than 36 per cent. of the latter metal it is termed *electrum*. Native gold usually also contains traces of iron and copper, as well as some of the metals of the platinum group. An amalgam of gold also occurs in nature. Gold is likewise found in the following combinations: bismuth-aurite, Au_2Bi; calaverite, $AuTe_2$; sylvanite or graphic tellurium, $(AuAg)_2Te_3$; nagyagite or black tellurium, $(PbAu)_2(TeSSb)_3$.

[1] Those interested in the processes employed by the alchemists in the search after the philosopher's stone are referred to Thomson's *History of Chemistry* and Berthelot's *Collection des Anciens Alchimistes Grecs.* (Paris, 1887-8.)

Traces of gold occur in many pyrites, blendes, and other ores. It has also been found in sea-water.[1]

Native gold is generally found *in situ* in quartz-veins or reefs which intersect metamorphic rocks, and to some extent also in the wall-rock of these veins. Metamorphic rocks which are thus intersected are generally chloritic, talcose, and argillaceous schists; also, though less commonly, mica- and hornblende-schists, gneiss, diorite, and porphyry, and, still more rarely, granite. Gold is frequently found crystalline, the commonest forms being the octohedron and tetrahedron. The crystals are, however, sometimes acicular, through elongation of these two forms, passing into filiform, reticulated, and arborescent shapes and occasionally exhibiting a spongy form from the aggregation of filaments. It frequently occurs in masses termed nuggets, also in thin laminæ, and often in flattened grains or scales and in rolled masses in sand or gravel. Sometimes indeed it is so finely disseminated throughout the quartz that it is not visible, though present in quantities sufficient to pay for its extraction.

The occurrence of gold is not confined to the above-named rocks, the metal being found in many formations, even up to the chalk.

The sands, gravels, and clays formed by the disintegration of the gold-bearing rocks form one of the most important sources of the precious metal, and these alluvial deposits often occur of considerable thickness and of great extent, those of the Yuba, an affluent of the Feather River in California, varying from 80 to 250 feet in depth and averaging probably 120 feet.

The relative amount of gold present both in the quartz-veins and the alluvial deposits is extremely small, varying from one part in 70,000 in the quartz to one in 1–15 millions in alluvium.

181 Although gold occurs widely distributed in nature it is only found in certain places in quantities sufficient to repay the process of extraction. The most important European localities are Hungary and Transylvania. These formerly yielded a considerable portion of the gold which came into commerce; but their importance as gold-bearing localities has recently much diminished. Gold is also found in the Alps, but the mines there, which were worked from the times of the ancients, are now altogether abandoned or worked but very slightly. Thus, for instance, at Zell in the Zillerthal in the Tyrol, and at Vöröspatak in Transylvania, gold-mining is still carried on.

[1] Liversidge, *Trans. Roy. Soc. N.S. W.* 1896.

The sands of all the rivers which flow from the Alps contain gold. Thus, for instance, the sands of the Upper Rhine have for centuries been washed for gold although the richest portion of the sand contains only about 56 parts of gold to 10 million. Gold has also been found in many streams in Cornwall, and the precious metal is now being worked to a considerable extent in North Wales. Gold has also been found in Scotland, especially near Leadhills, and in Glencoich and other parts of Perthshire, in Ireland in County Wicklow, in Sweden, and in Spain, where mines were worked by the Romans. In Asia gold occurs chiefly on the eastern flanks of the Urals and in other parts of Siberia, but the metal has been found in almost all parts of this continent, especially in India and Corea. The vessels of gold in the possession of the ancient Scythians, which according to Herodotus were said to have fallen from the skies, were probably made from Uralian gold. The mines in the Urals were however not opened until the year 1819, but they soon became of such importance that they supplied the greater portion of the world's requirements until the discovery of Californian gold.

Africa also contains much gold. Thus a considerable quantity of gold-dust has been found in Abyssinia, also on the coast opposite Madagascar, supposed to be the *Ophir* of Solomon, and in various parts of the interior of the western portion of the continent whence it was formerly sent to the gold-coast. Indeed this source, together with that of Hungary and the Brazils, yielded the chief supply of gold up to the beginning of the present century.

Since the year 1884, the gold-fields of the Transvaal have become of great importance, the output having risen continuously since that date. In 1892 the amount of gold obtained from the Rand district was 1,210,867 ozs., whilst in 1895 it had increased to 2,277,635 ozs. Africa is now only second to Australasia in its production of gold, and will most probably soon surpass it.

182 Since the year 1849 gold-bearing regions have become known which in richness far surpass all those hitherto known. In that year gold was discovered in California by Colonel Sutter, who having erected a saw-mill noticed that the water which was to work the mill contained particles of gold. The attempt to keep this discovery secret naturally failed, and the few hundred inhabitants of the city of San Francisco rushed to the gold-

diggings, and were soon followed by emigrants from all parts of the world. For the first few years Californian gold was obtained entirely from alluvial washings, but since 1852 true gold-mining has been on the increase. The gold-bearing quartz-reefs are often very large. Those on the Mariposa estate average twelve feet, but in some cases extend to 40 feet in breadth.[1] Besides those of California, other considerable gold-fields exist in the western portion of the North American continent, reaching from Mexico up to British Columbia.

183 Australia is another country especially rich in gold-fields. Important gold-mines occur in the table-lands of New South Wales and along the continuation of the Australian cordillera in Victoria, in Queensland and Western Australia, whilst smaller supplies are drawn from South Australia and Tasmania.

It is a matter of general notoriety that many years before anything was published respecting the existence of gold in Australia, gold was often brought into Sydney by shepherds and settlers in the bush. The actual occurrence of gold in Australia was, however, first discovered by Count Strzelecki in the year 1839, but this was not made known at the time, inasmuch as the Governor feared the consequences of such a statement in the then condition of the colony. In 1843–4 Count Strzelecki returned to England and exhibited his nuggets and gold specimens to Sir Roderick Murchison, who, arguing from the comparison of the geological features of these and the gold-bearing Urals, predicted that gold would be found widely distributed in the eastern chains of the Australian mountains. In the years 1841–3 gold was also found by the Rev. W. D. Clarke, an Australian geologist. To Mr. Hargreaves, an old Californian gold-digger, however, belongs the honour of proving, in 1851, that gold exists in large quantities in various parts of the colony, and of showing how it can be readily obtained from alluvial deposits by means of the cradle. The first discovery of workable gold-fields was made at Ophir, and this soon led to the finding of the precious metal in the soil and rocks of the colony over tracks many miles in extent. After a short time the proclaimed gold-fields extended, with a few intervals, the whole length of the colony, and westward about 200 miles, comprising an area of about 1,356 square miles, and numbering more than eighty distinct fields.[2]

[1] See J. D. Whitney's *Geology of California*.

[2] Liversidge, *Trans. Roy. Soc. N.S.W.* ix. 153.

Gold has also been found in New Zealand and New Caledonia. The Australian is, as a rule, much purer than the Californian gold, but it is a singular fact that the average fineness of the gold found in the several Australian colonies shows a regular depreciation as we advance northwards. Thus the average fineness of Victorian gold is about 960; that of the New South Wales gold is 935, while still further north in Queensland the average fineness is 872, and Maryborough gold contains only 85 per cent. of gold and as much as 14 per cent. of silver.[1] Very large nuggets occur in Australian fields; thus, for instance, one found at Ballarat weighed 184 pounds and was valued at £8,376 10*s.* 6*d.*

The production of gold reached a very high mark in the fifties when the Australian discoveries followed on the opening of the Californian fields. During these years the annual production averaged £30,000,000, but afterwards gradually fell off, until in the period 1880–90 it only averaged about £20,000,000. Since that date it has again increased, chiefly because of the great increase in the output from Africa consequent upon the development of the Transvaal fields, and because of the improved methods employed for the extraction of the metal. The following figures (quoted from the Report of the United States Mint) give the production in ounces of fine gold from each of the great gold-producing countries for the years 1891–1894:

	1891.	1892.	1893.	1894.
Australasia . .	1,513,690	1,638,238	1,711,892	2,350,000
United States .	1,604,840	1,597,098	1,739,081	1,910,000
Russia	1,168,769	1,198,206	1,200,000	1,600,000
Africa	725,860	1,201,818	1,563,196	2,300,000
Other Countries .	1,085,293	1,115,182	1,160,090	2,119,200
Total . . .	6,098,452	6,750,542	7,374,259	10,279,200

Composition of Native Gold.—The table on the opposite page gives the composition of several kinds of native gold.

184 *Gold-mining.*—The simplest method of gold-mining, namely, *alluvial-washing* or *placer-digging*, as it is termed in California, carried on from the simple pan-washing to hydraulic mining on a stupendous scale, necessarily requires a considerable quantity of running water. This or a similar process was in use amongst the ancients; thus Pliny describes the "bringing of rivers from the mountains, in many instances for a hundred miles for washing the débris," &c., &c.

[1] F. B. Miller, *Trans. Roy. Soc. N.S.W.* 1870.

Locality.	Barbara (Siebenbürgen).	Katharinenberg (Ural).	Senegal.	Bolivia.	California	Australia.	Transvaal.
Analyst.	Rose.	Rose.	Levol.	Forbes.	Hunt.	Northcote.	Cohen.
Gold . .	84·80	93·34	94·40	94·73	89·24	99·28	94·48
Silver . .	14·68	6·28	5·85	5·23	10·76	0·44	5·16
Iron . .	0·13	0·32	—	0·04	—	0·20	Trace
Copper .	0·04	0·06	—	—	—	0·07	0·25
Platinum.	—	—	0·15	—	—	—	—
Bismuth .	—	—	—	—	—	0·01	—
	99·65	99·90	100·00	100·00	100·00	100·00	99·89

The washing apparatus is simple enough though frequently ingenious. The simplest of all these operations is that termed *pan-washing*, in which a shallow pan is used, of iron or zinc, sinking into a cavity in the middle in which the heavy particles collect, whilst the lighter dirt is washed away. The wash-dirt or wash-stuff is brought into the pan in a stream of running water and the mass well stirred up with the hand so that the larger stones and heavy particles are left whilst the mud flows over the edge of the pan. The gold, which is found when the stones are picked out, is usually mixed with magnetic sand; it is dried and then brought into a shallow dish and the black sand separated by blowing, the whole being kept in a state of constant rotation.

The *cradle* is another simple apparatus for gold-washing, much used in the early days of the gold discoveries in California and Australia. It consists of a trough or cradle of wood or iron six or seven feet in length under which rockers are placed, so arranged that the cradle has a slanting position to allow the mud and water to run off. At the top of the cradle is a grating or sieve upon which the wash-stuff is thrown, and transverse bars of wood are placed across the bottom of the cradle to arrest the passage of the heavier particles of gold. Four men are needed to work this efficiently; one digs out the auriferous wash-stuff, another brings it to the cradle, a third rocks the trough, and the fourth attends to the proper supply of water and the uniform washing of the material.

185 *Hydraulic Gold-mining.*—The system of hydraulic mining carried out in California on a stupendous scale will best be understood by the following quotation from Professor Silliman :—

As the shallow placers in the ravines and river-beds in California became exhausted, the necessity for adopting a method for economically working the deep placers was felt. This has been done by the introduction of hydraulic mining, requiring the construction of canals and aqueducts to convey water from the fountain-heads to the ground to be worked, as well as the opening of tunnels and shafts in the bed-rock, in which the gold occurs, for the discharge of the gravel. The capital and labour expended on these works in California since the year 1853 has been enormous. In order to work the process satisfactorily the whole mass of the auriferous gravel must first be moved quite down to the bed-rock. This must be accomplished by water alone, and the whole compact conglomerate must be thus mechanically disintegrated whilst the gold is deposited and collected in the process of washing. These conditions are in practice met by the following arrangement. The mining ground having been selected, a tunnel is projected from the nearest and most convenient ravine, so that starting in the bed-rock on the face of the ravine it shall approach the centre of the gravel mass to be moved at a gradient of from 1 in 12 to 1 in 20. This tunnel is usually six feet wide and seven feet high and varies in length from a few hundred feet to many thousands. The end of the tunnel is arranged so as to be from 50 to 100 or more feet below the under surface of the gravel. At this point a shaft is sunk through the gravel and bed-rock until it intersects the tunnel. Throughout the length of the tunnel sluice-boxes are laid so as at once to direct the stream of water and to save the gold. For this purpose a trough of strong planks is built in the tunnel $2\frac{1}{2}$ feet wide, the bottom of which consists of blocks of wood placed about two inches apart, and in the interstices thus left a small quantity of quicksilver is placed to aid in catching the heavy particles of gold which fall into these hollow places. The water from the canal is brought by aqueducts to the head of the mining-ground with an elevation of 100 to 400 feet above the bed-rock, and it is conveyed into the bottom of the mining claims by iron pipes sustained on timbers. These communicate at the bottom with a strong box of cast-iron, at the top and sides of which are openings for the adaptation of flexible pipes which end in nozzles sometimes of three to five inches in diameter, from which a stream of water issues under great pressure and with immense force, and these are allowed to play, as is seen in Fig. 88, on the surface of the auriferous

conglomerate. Under the continuous action of this enormous mechanical force aided by the softening power of water, large sections of the mass come crashing down with great violence; the débris, quickly disintegrating and disappearing under the resistless force of the torrent of water, is hurried forward to the mouth of the shaft down which it is precipitated with the whole volume of turbid water. This then finds its way down the tunnel which is cleared at intervals of from ten to twenty days, the whole of the pavement of the blocks being removed and the amalgam of gold and "rich dirt"

Fig. 88.

contained in the interstices taken out, the blocks replaced, and the operation continued. Rude as this method of saving the gold appears, experience shows that more gold is saved by it than by any other method of washing yet devised, while the economical advantages it offers are incomparably greater than any other. Indeed it would be absolutely impossible to handle so vast a body of poor material in any other way now known. To show the enormous advantage gained by the present system of working compared with those formerly in use, Mr. Black, a Californian engineer, states that taking a miner's wages at four

dollars a day, the cost of handling a cubic yard of auriferous gravel is as follows:

With the pan	20	dollars.
„ „ rocker	5	„
„ „ long tom . . .	1	dollar.
„ „ hydraulic process	0·2	„ [1]

186 *Quartz-mining.*—The mining operations carried on in the gold-bearing quartz-reefs are not different from those used in the case of other ores. In order to extract the gold from the gangue the whole mass must be well pulverised, and the gold extracted from the powdered ore by means of mercury. The quartz is fed into a cast-iron mortar along with water, and is there crushed by means of a heavy iron or steel stamp. The pulp is discharged through screens of steel or brass wire or punched iron sheeting, and then passes over a series of amalgamated copper plates, the exhausted tailings being either discharged or preserved for further treatment by the cyanide process. Mercury is often placed inside the mortar, and the upper portions of the sides of the latter are lined with amalgamated copper plates. The gold amalgam produced is removed from time to time, cleaned, strained through wash-leather and then heated in iron retorts, the porous gold which remains being melted and cast in iron moulds. Many methods have been proposed for the purpose of promoting the amalgamation of the gold contained in the crushed ore, among these being the application of sodium amalgam, and of nascent hydrogen, produced by electrolysis (Molloy's hydrogen amalgamator), &c., but none of these has come into general use. It is essential that the surface of the mercury be kept as free as possible from grease.[2]

187 *Gold Extraction by Chlorine.*—For the purpose of extracting gold from auriferous pyrites Plattner's chlorine method is sometimes employed. In California the "tailings" and deposited auriferous pyrites are roasted in order to remove the sulphur and arsenic and to render the ore porous, then moistened with water, and placed in tubs furnished with false bottoms, beneath which chlorine is introduced. After all the air has been replaced by chlorine, and the whole mass has become impregnated

[1] B. Silliman. "On the Deep Placers of the South and Middle Yuba, California," *Amer. Journ. Sci. and Art*, [2], xl. 1.

[2] Full information concerning the metallurgy of gold may be found in *The Metallurgy of Gold* by Rose (Griffin & Co., 1894).

with this gas, the tubs are allowed to stand for about twelve hours. After the lapse of this time the soluble gold chloride is washed out with water.

In some cases the chlorination is carried out in revolving lead-lined steel barrels or cylinders, the chlorine being produced by the action of sulphuric acid on bleaching powder placed inside the barrel. In this way a pressure of about two atmospheres is produced, and a charge of $3\frac{1}{2}$ tons is chlorinated in an hour and a half. The gold chloride solution is filtered through an asbestos cloth placed inside the barrel and passes directly into the precipitation tank. The metal may be precipitated from the solution by a number of different substances, the chief of which are ferrous sulphate, sulphuretted hydrogen, solid charcoal and sulphide of iron or copper; the reaction being as follows in the case of ferrous sulphate :—

$$AuCl_3 + 3FeSO_4 = Au + FeCl_3 + Fe_2(SO_4)_3.$$

Sulphuretted hydrogen and metallic sulphides precipitate a sulphide of the metal, whilst charcoal precipitates the metal, and is itself partially oxidised to carbonic acid. The precipitate is collected, dried, roasted if it consist of the sulphide, and the metal then fused with borax.[1]

It has also been proposed to employ bromine, either as bromine water or sodium hypobromite, for the extraction of the gold.

188 *The MacArthur-Forrest Cyanide Process.*—Finely-divided gold dissolves readily in a weak solution of potassium cyanide in the presence of atmospheric oxygen, a soluble double cyanide being formed :—

$$4\,Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH.$$

This reaction is now employed on a very large scale for the extraction of gold from the tailings obtained from the stamp batteries, which only contain a small amount of metal, and from such low-grade ores as contain the metal in a very finely divided condition. In the Transvaal the gold-containing material is placed in large vats provided with false bottoms and is treated with a weak solution of potassium cyanide containing 0·6–0·8 per cent., which is allowed to remain in contact with the ore for from 6 to 12 hours, and is then drawn off and replaced by a weaker solution (0·2–0·4 per cent.). The ore is finally washed with water

[1] *Journ. Soc. Chem. Ind.* 1896, 336.

and discharged. The cyanide solution passes into wooden troughs containing freshly-turned zinc shavings, which effect the precipitation of the gold:

$$2KAu(CN)_2 + Zn = 2KCN,Zn(CN)_2 + 2Au.$$

The gold, together with any silver, &c., present in the ore, falls to the bottom of the trough and is removed and melted in graphite crucibles with sand, borax and sodium bicarbonate. The metal thus obtained contains about 60 per cent. of gold, 7 per cent. of silver, and 10 per cent. of zinc, together with smaller quantities of lead, copper and iron. The rapidity with which the gold dissolves does not appear to depend so much upon the concentration of the solution of potassium cyanide, as upon the temperature; it becomes much greater when the temperature is raised. The process cannot be economically applied to ores containing less than about $1\frac{1}{2}$–4 dwts. of gold per ton.

189 *Refining and Parting of Gold.*—The gold bullion obtained by the above processes varies very considerably in composition, according to its origin and the treatment to which it has been subjected. It usually contains a considerable amount of silver along with copper, iron, lead, antimony and other base metals. When the amount of these is at all considerable it is usual to submit the bullion to a preliminary refining process before removing the silver. This is done by melting the metal in a graphite or clay crucible with borax and nitre, the base metals being thus oxidised and removed by skimming.

The parting of silver from gold was formerly carried out by means of nitric acid, this process having been first employed, it would appear, at Venice in the fifteenth century, for extracting the gold from Spanish silver. It remained in general use up to the beginning of this century and is still frequently employed. It depends on the fact that nitric acid removes practically all the silver from an alloy of gold and silver, provided that a sufficient excess of silver be present. It was at first thought that the limiting proportion was 1 of gold to 3 of silver, and hence the process was termed *inquartation*, but it has been found that the method succeeds even when as much as 1 of gold is present to 2 of silver.

Parting by Sulphuric Acid.—In 1753 Scheele discovered that sulphuric acid could be employed for this purpose. In a memoir on the subject, read before the Stockholm Academy, he says: "Sulphuric acid also dissolves silver when no water is amongst

it, but gold is not in the least degree altered, so that silver and gold can be thus completely separated from one another; but such an oil of vitriol is much dearer than nitric acid, and for this reason it is not advisable to use it for this purpose, as there are other acids which cost less." Hence it was only when sulphuric acid became cheaper that the process of separation by its means could be carried out, and this was done by Darcet in 1802.

In order to separate the two metals by this method the alloy must not contain more than 25 per cent. of gold. If it be richer than this, it must be first melted with the necessary quantity of silver. The granulated alloy is heated in cast-iron boilers, together with two and a half times its weight of concentrated sulphuric acid of specific gravity 1·85. Each vessel is covered with a dome of lead, and the sulphur dioxide which is evolved during the solution of the silver is either allowed to escape into the air or led into sulphuric acid chambers. As soon as no further evolution of this gas takes place, sulphuric acid, of specific gravity 1·69, is added for the purpose of dissolving the copper vitriol. The clear liquid is then allowed to flow into leaden pans containing the mother-liquors of copper vitriol formed in the next operation, and the whole is heated by steam in order to keep the slightly soluble silver sulphate in solution. Here a further quantity of gold is deposited, the clear liquid is again drawn off, and the silver precipitated by means of metallic copper. The finely-divided gold is again treated with sulphuric acid in a platinum vessel in order to render it completely free from silver, and after having been well boiled, it is washed and fused in a black-lead crucible with sodium bicarbonate.

In a modified form of the process, the sulphuric acid solution of the silver is diluted with steam and the silver sulphate Ag_2SO_4, allowed to crystallise out. The crystals are then removed and reduced by heating in a furnace with charcoal.

Parting by Chlorine.—The gold employed for coinage, when it does not contain more than 10 per cent. of silver, is now usually purified by Miller's process with chlorine gas, first introduced by him in the Sydney Mint. This process consists in melting the gold in a clay crucible which has been glazed inside with borax, and passing chlorine gas through the molten metal by means of a clay pipe. The chlorine at once combines with the silver to form silver chloride, which rises to the surface of the molten metal, whilst the chlorides of zinc, bismuth, antimony, and arsenic, should these metals be present, are volatilised

and the pure gold remains beneath. A layer of melted borax is placed on the top of the fused mass in order to prevent the silver chloride which is formed from being volatilised. The fineness of the gold thus prepared varies from 991 to 997 in 1,000 parts, whilst the metal obtained by other refining processes frequently contains a larger quantity of silver. This method of treatment may also be adopted with advantage for refining and toughening gold which is rendered brittle by the presence of small quantities of antimony, bismuth, tin, arsenic, &c.[1]

190 *Preparation of Pure Gold.*—In order to prepare gold containing less than one part of impurity in 10,000, gold cornets are dissolved in aqua-regia, the liquid evaporated down and traces of platinum removed by the addition of potassium chloride and alcohol. The clear solution of gold chloride is then allowed to stand, decanted from any precipitated chloride of silver, and reduced by warming with oxalic acid. The precipitate is repeatedly washed with hydrochloric acid, water and ammonia, and is then fused in a clay crucible with potassium bisulphate and borax.

191 *Properties.*—Gold is distinguished from all the other metallic elements by its bright yellow colour. It crystallises in the regular system, and in the native state is often found in distinct though small crystals. Some Australian gold worth about £1,100 consisted of grains from the size of a large pea to that of small grains of sand, all of which were more or less perfect dodecahedra.[2] Native gold has also been found crystallised in a very great variety of other forms of the regular system.[3] These small crystals are frequently connected together, so as to form hair-like filaments, termed *moss-gold.* Liversidge[4] has obtained this form of gold artificially. He noticed the occurrence of crystallised gold in certain specimens of Australian auriferous pyrites, and he therefore roasted this mineral in a muffle, for the purpose of removing arsenic and sulphur, but at a temperature insufficient to bring about the fusion either of the mineral or of the gold. On removing the sample from the muffle, small cauliflower-like excrescences of metallic gold were observed on the surface of the mass, these excrescences being composed of fine filaments of the metal often wound round in spiral coils.

[1] Roberts-Austen, *First Annual Report of the Mint*, 1870, 95.
[2] Dana, *System of Mineralogy*, 5 Ed. p. 8.
[3] G. von Rath, *Zeitsch. Krystall. Mineralog.* **1**, 1.
[4] *Proc. Roy. Soc. N.S. Wales*, 1876, 125.

Gold precipitated from a concentrated solution by ferrous sulphate forms very small cubes, and that obtained by reduction with oxalic acid consists of minute octohedra, which are usually much distorted. When an amalgam containing 5 per cent. of gold is heated for eight days to 80°, and then treated with hot nitric acid, an aggregate of crystals, some of which are 6 mm. in length, may be obtained. These, after heating to get rid of the mercury, have a bright lustrous appearance.

Gold is softer than silver, and is the most ductile of metals. This was known to Pliny, who says: "Superque omnia netur, ac texitur lanæ modo." [1]

Although the relation which the Roman weights and measures bear to those in use in the present day is still somewhat uncertain, the following statement may be of interest as showing the progress of the art of gold-beating. In the first place we read in Pliny, "nec aliud laxius dilatatur, aut numerosius dividitur, ut pote cujus unciæ in septingenas et quinquagenas, pluresque bratteas, quaternum utroque digitorum spargantur." [2] Then in 1621 Mersenne mentions that the Paris gold-beaters were in the habit of obtaining 1,600 leaves from one ounce of gold, which would cover 105 square feet. In 1680 Halley states that in his time a grain of gold could be drawn into a wire 98 ells in length, whilst Reaumur mentions in 1711 that one ounce of gold can be hammered out so as to cover 146½ square feet, and according to newer statements one grain may be made to cover 56·75 square inches, or one ounce to cover 189 square feet, whilst 280,000 leaves have to be placed one upon another to occupy the thickness of one inch. One grain of gold also serves to gild two miles of fine silver wire, whilst the thickness of such deposits of gold as, for example, that on gold lace is about 0·000002 mm. Gold is extremely ductile, and gold wire can be drawn so fine that 3,240 metres weigh only one gram. Gold-leaf has usually a thickness of about 0·0001 mm., and allows green light to pass through. Metallic gold can be precipitated in a dilute liquid in so fine a state of division that it remains suspended, and under these circumstances it appears by reflected light, of a purple-red, whilst by transmitted light it assumes a blue colour.

The relations of finely-divided gold to light have been carefully

[1] *N.H.* **33**, 19.

[2] *N.H.* **33**, 19. An ounce of gold can be hammered into 750 leaves, each of which is 4 digits (about 3 inches) square.

examined by Faraday.[1] By spreading a leaf of gold on a glass-plate and then pouring on to it a solution of potassium cyanide, Faraday succeeded in obtaining films of gold of extreme tenuity. The green colour which ordinary gold-leaf exhibits by transmitted light passes into a ruby-red when the highly attenuated film is heated to 316°. The red colour of ruby glass is due to the presence of metallic gold in an extreme state of division. This is also the case with the above-mentioned film, the original green tint of which can be brought back by burnishing its surface.

At 13° gold has a specific gravity of 19·265 (Matthiessen), whilst strongly compressed gold has the specific gravity 19·5; it fuses at 1061·7°,[2] expanding considerably in the act of fusion, and forming a bluish-green liquid. It volatilises at a very high temperature, as when auriferous platinum is fused in the oxy-hydrogen blowpipe, or when a powerful electric discharge is passed through a thin gold wire, and loses weight perceptibly even at temperatures only 100° above its melting point.[3]

Gold has the specific heat 0·0324; it is only exceeded in conductivity for heat and electricity by silver and copper, its electrical conductivity being 76·7 and its thermal conductivity 53·2 per cent. of that of silver.

Gold is not attacked at any temperature either by oxygen or by water, and it also remains unacted upon when fused with potassium chlorate. Alkalis and the nitrates, however, attack it. Gold does not dissolve in any simple acid, with the exception of selenic (Mitscherlich) and iodic, but it dissolves readily in aqua-regia, or in any acid liquid in which chlorine or bromine is evolved, and in solutions of the easily decomposable per-halogen compounds of the metals, such as $FeBr_3$, $CoCl_3$, &c.

192 *Purple of Cassius.*—This body, which is used in the preparation of ruby glass, was discovered by Andreas Cassius, who, however, did not publish anything on the subject, though his son of the same name published a pamphlet in 1685 entitled, *De extremo illo et perfectissimo naturæ opificio ac principe terrenorum sidere, Auro, et admiranda ejus natura—cogitata, experimentis illustrata.* In the previous year however, a Hessian mining official, Orschal, published a paper, *Sol Sine Vesta: or, Thirty Experiments to Draw out its Purple*

[1] *Phil. Trans.* 1857, p. 145.
[2] Heycock and Neville, *Journ. Chem. Soc.* 1895, i. 189, 1024.
[3] Rose, *Journ. Chem. Soc.* 1893, 714.

from Gold. He declared that he had learned the process from Cassius, and that it consisted in precipitating gold with tin. After that time many investigations were made on this pigment without any satisfactory explanation of its chemical nature being arrived at. A variety of receipts was given for its preparation, in all of which gold chloride was precipitated by a mixture of stannous and stannic chlorides. This precipitate is, according to the mode of preparation, either of a dark purple-red or of a reddish-brown colour, both yielding a brown powder on drying. The process by which the finest purple is obtained is, according to Fuchs, to add stannous chloride to a solution of ferric chloride until the yellow colour is changed to a pale green, and then to precipitate the gold solution with this mixture. The precipitate contains tin oxide in varying quantities, and some chemists have supposed that the compound is a gold stannate, but this view is contradicted by the fact that when purple of Cassius is dried and then triturated, the powder assumes a metallic lustre, and on heating does not evolve oxygen. For this reason others have regarded the substance as a mixture of tin oxide and very finely-divided gold. On the other hand, it is found that the freshly precipitated and moist pigment is soluble in ammonia forming a purple-coloured liquid, which deposits gold when it is exposed to light or heated ;[1] the excess of ammonia can also be removed by dialysis leaving a colloidal solution of gold and stannic oxide.[2] Moreover, mercury does not extract gold from purple of Cassius. It has been suggested that the gold is present in an allotropic form. The literature respecting the purple of Cassius has been collected by J. C. Fischer.[3]

193 *Gilding.*—The art of gilding is mentioned by Moses, and Pliny states that objects of wood and marble are gilt by means of gold-leaf, whilst metallic surfaces are gilt by help of quicksilver. Gold-leaf is obtained from gold-foil by hammering pieces, each having an area of a square inch and weighing six grains, first between sheets of vellum or tough paper, and afterwards between leaves of gold-beater's skin—a material prepared from the cæcum of the ox. The small cuttings and waste leaf are employed for the preparation of the shell gold used by painters.

[1] See also Müller, *J. Pr. Chem.* 1884, [2], **30**, 252.
[2] Schneider, *Zeit. Anorg. Chem.* 1893, **5**, 80.
[3] *Dingl. Polyt. Journ.* 1866, **182**, 39.

A variety of methods is employed for gilding metals. In gilding by immersion the well-cleaned objects are dipped into a boiling solution of gold chloride and potassium bicarbonate; whilst in wash-gilding a gold amalgam is rubbed on the surface, the mercury afterwards driven off by heating, and the surface either burnished, or deadened by heating it with a fused mixture of common salt, saltpetre, and lime, when a small quantity of chloride is liberated which etches the gold. These older methods have now, however, been almost completely supplanted by the *electro-deposition of gold.* For this purpose a solution of gold cyanide in potassium cyanide is employed, a gold plate being used as the positive electrode. The colour of the deposited gold can be modified by adding to the gold solution salts of silver or copper, as well as both of these, when alloys are deposited.

194 *Alloys of Gold.*—Pure gold is very soft, and is soon worn away by use. Hence, for the purpose of coinage, and for the use of the goldsmith, it is alloyed with copper or silver, or with both together, the resulting alloys being much harder than pure gold. Copper imparts to the gold a red colour, and lowers its fusing-point. This alloy was formerly called red-carat gold, because the fineness of a gold alloy used to be universally expressed in carats, 24-carat gold being pure gold. In England at the present time five legal standards exist for gold ware; 22-carat, or standard gold, 18, 15, 12, and 9-carat gold, the meaning of this being that 24 parts by weight of the alloy contain 22, 18, 15, 12, and 9 parts of gold respectively.

In the case of the coinage, however, the fineness of gold is generally expressed in parts per 1,000. Thus, for instance, English standard gold, being a 22-carat gold, has a fineness of 916·66. In the German, American, and Italian coinage standard gold is of 21·6 carats, or has a fineness of 900. Red-carat ornaments are frequently covered with a thin coating of pure gold by heating them and dipping them for a short time in dilute nitric acid.

The alloys of gold and silver are called white alloys, and have a greenish-yellow colour if they do not contain too small a quantity of silver, whilst when the latter metal is present in larger amount the alloy assumes a yellowish-white shade. A gold-silver alloy of varying composition occurs naturally as electrum, often found in crystals belonging to the regular system, and numerous crystalline alloys, such as AuAg, $AuAg_2$, Au_2Ag, have been artificially obtained.

Trinket gold contains both copper and silver. It is hard, and, according to the proportion of its materials, possesses either a yellowish-red or a whitish colour.

Various other alloys have been examined and described. Of these the aluminium-gold alloys are distinguished by the richness and variety of their colours.[1]

Gold also combines with arsenic, antimony and bismuth when heated with these elements. The addition of 1 part of the last-named metal to 1,920 parts of gold is sufficient to render the gold brittle.

Gold-Amalgam.—Gold readily combines with mercury, the mixture becoming solid when 15 per cent. of gold is present. Crystalline amalgams of varying composition can be obtained artificially, whilst others occur naturally in California, Columbia and Victoria. The mercury may be almost entirely removed from these amalgams by distillation at a red-heat.

COMPOUNDS OF GOLD.

195 Gold forms two chief series of compounds, the auric compounds in which it is trivalent, and the aurous compounds in which it is monovalent. The best known salts are those of the halogen acids, and hydrocyanic acid. These readily form double salts, as do aurous sulphite and thiosulphate. Auric oxide has well marked acidic properties, as have also the various sulphides of the metal. The compounds with the halogens, oxygen and sulphur, are all decomposed into their elements by heat, whilst reducing agents very readily precipitate the metal from the solutions of its salts.

Gold and Oxygen.

196 Gold does not combine directly with oxygen, and the two compounds, aurous oxide, Au_2O, and auric oxide, Au_2O_3, are obtained from the corresponding halogen compounds. A third compound, auroauric oxide $(AuO)_n$, is formed by the partial decomposition of auric hydroxide at 160°. The substance formerly known as purple oxide of gold appears to be nothing but finely-divided gold, and the oxides Au_2O_4,[2] and Au_2O_5,[3] appear not to

[1] Roberts-Austen, *Proc. Roy. Soc.* 1892, 367.
[2] Prat, *Compt. Rend.* 1870, **70**, 842.
[3] Figuier, *Ann. Chim. Phys.* (2), **44**, 167.

exist. All the oxides decompose into gold and oxygen when they are heated. Auric oxide acts towards bases as an acid-forming oxide, whilst it also forms salts with acids.

Gold Monoxide, Aurous Oxide, Au_2O.—The hydroxide, AuOH, is formed when the corresponding chloride is treated with cold dilute caustic potash (Berzelius), and when a solution of the trichloride is boiled with the potassium salt of acetic or another organic acid. It may be prepared pure by reducing potassium auribromide, $KAuBr_4$, with sulphurous acid, and then warming with dilute potash. It is a powder which when moist has a dark-violet colour, and becomes greyish-violet when dry. When freshly prepared it dissolves in cold water, yielding an indigo-blue solution.[1] It loses water at 200°, and is decomposed at 250° into gold and oxygen. When treated with hydrochloric acid, it yields gold and the trichloride, slowly in the cold, more rapidly on boiling. Sulphuric acid and nitric acid do not act on it, but it is easily dissolved by aqua regia.

Gold Trioxide, Auric Oxide, Au_2O_3.—The substance termed calx of gold by the early chemists was nothing more than the finely-divided metal. Bergman was the first to state that the precipitate produced by alkalis in the gold solution was dephlogisticated gold; but the oxide was examined more carefully in 1806 by Proust, and in 1811 by Oberkampf. Gold trioxide is a brownish powder, obtained by carefully heating the hydroxide. If this be more strongly heated, it gives off oxygen, and is converted into a brown powder of metallic gold.

Gold Trihydroxide, Auric Hydroxide, $Au(OH)_3$, is best obtained by heating a solution of gold trichloride with an excess of magnesia, and well washing the precipitate with dilute nitric acid (Pelletier). The gold solution may also be treated with caustic potash until the precipitate which is formed is redissolved, and then the dark-brown solution boiled until it becomes of a light-yellow colour, a slight excess of sulphuric acid added, and the precipitate washed. The hydroxide thus prepared always contains a little potash, and for this reason it is dissolved in concentrated nitric acid, again precipitated by water, and dried in a vacuum. According to Thomsen a better method is to precipitate the brown solution by Glauber's salt, when it is obtained in a form resembling precipitated ferric hydroxide. Gold trihydroxide when kept over phosphorus pentoxide is converted into a

[1] Krüss, *Ber.* 1886, **19**, 2541.

chestnut-brown powder of *auryl hydroxide*, AuO(OH), which at 140—150° yields auric oxide (Krüss).

When the hydroxide is warmed with alcoholic potash the metal is reduced in the form of fine glistening scales, which are employed in miniature painting. It is a weak base, which dissolves slightly in concentrated sulphuric acid, and more readily in nitric acid, from which solutions it is again precipitated on the addition of water. It forms the corresponding haloid salts with hydrochloric and hydrobromic acids. Gold trioxide is also an acid-forming oxide, and its salts are termed aurates.

Potassium Aurate, $KAuO_2 + 3H_2O$, is obtained in the form of small yellow needles by evaporating a solution of auric hydroxide in caustic potash in a vacuum; these are easily soluble in water and have a strong alkaline reaction. It is very unstable, and its solution is used for gilding copper and other metals.

The other aurates are less completely investigated. The solution of the potassium salt yields precipitates with many metallic salts.[1]

Auroauric Oxide, $(AuO)_n$, is formed when auric hydroxide is heated at 160°. It is a dark yellowish-brown hygroscopic powder which loses oxygen at 173°.[2]

Gold and the Halogens.

197 Gold unites with chlorine and bromine directly to form the auric compounds, $AuCl_3$, $AuBr_3$, which are easily soluble in water. These readily combine with the halogen acids and their salts with monovalent metals or radicals to form complex substances such as aurichloric acid, $HAuCl_4$, and the aurichlorides. The salts of this acid with the organic bases such as methylamine aurichloride, $N(CH_3)H_3\,AuCl_4$, are often used for the characterisation of the latter. Both the halogen compounds themselves and their compounds with the corresponding acids decompose when heated, metallic gold being finally left.

The aurous compounds are unstable and readily decompose when heated. They are insoluble in water, like the corresponding silver and cuprous compounds.

The substances described as auroauric chloride and bromide,[3]

[1] Fremy, *Ann. Chim. Phys.* 1851 (3), **31**, 480.
[2] Krüss, *Ber.* 1886, **19**, 2541.
[3] Krüss and Schmidt, *Ber.* 1887, **20**, 2634; *J. Pr. Chem.* 1888, (2), **38**, 77.

Au_2Cl_4 and Au_2Br_4, have been proved to be nothing but mixtures of metallic gold with the corresponding auric salt.

Aurous Chloride, AuCl, is best obtained by carefully heating the trichloride to about 185°. It is a yellowish powder of specific gravity 7·4,[1] which decomposes gradually into gold and chlorine at 185°, more rapidly at a higher temperature.

It is insoluble in water but is decomposed by it slowly in the cold, more rapidly on heating with formation of metallic gold and auric chloride.

Potassium Aurous-chloride, $KAuCl_2$, is formed when potassium aurichloride, $KAuCl_4$, is heated. It forms a yellow mass, which is decomposed by water into gold, potassium chloride and auric chloride.

Auric Chloride, or *Gold Trichloride*, $AuCl_3$.—The Latin Geber and all the later chemists were acquainted with the fact that gold dissolves in aqua-regia. When this solution is evaporated to dryness a portion of the chloride is decomposed with formation of aurous chloride (Berzelius). In order to prepare the pure anhydrous chloride the best process is that proposed by Thomsen. It consists in acting upon gold powder with chlorine and treating the mass with a small quantity of water. When gently heated, any aurous chloride decomposes as before described, the metallic gold is filtered off, the solution evaporated gently, and then heated to 150°, when anhydrous auric chloride remains as a brown crystalline mass which is soluble in ether. The anhydrous chloride is also formed by heating gold-leaf in chlorine to 300°. It melts at 288° when heated in a sealed tube, and has the sp. gr. 4·3. When the brownish-red aqueous solution is evaporated down until a crystalline film is formed on the surface, large dark orange-red crystals of $AuCl_3 + 2H_2O$ are deposited. These deliquesce in moist air, whilst they effloresce in dry air.

The chloride dissociates very slowly below 100°, more rapidly at higher temperatures, with formation of aurous chloride, chlorine and gold. The dissociation pressure of the chlorine is about 1 atmosphere at 251°, and 4 atmospheres at 330°. In spite of this dissociation the chloride can be sublimed in a stream of chlorine at all temperatures up to 1,100°, the most rapid volatilisation taking place at the melting point.[2]

[1] Rose, *Journ. Chem. Soc.* 1895, 881, 905.

[2] Debray, *Compt. Rend.* 1869, **69**, 985; Krüss, *Annalen*, 1887, **238**, 249; *Ber.* 1887, **20**, 2634; Rose, *Journ. Chem. Soc.* 1895, i. 881.

Aurichloric Acid, $HAuCl_4$.—When hydrochloric acid is added to a neutral solution of auric chloride it becomes yellow, and the liquid then contains the above compound in solution. The same substance is obtained when gold is dissolved in aqua-regia containing an excess of hydrochloric acid. When either of the above solutions is evaporated and allowed to stand over quicklime, long yellow needles of $HAuCl_4+3H_2O$ are deposited, which deliquesce on exposure. The solution has a bitter taste, is poisonous, and colours the skin, nails, ivory, &c., of a purple-red tint when exposed to light. This fact was mentioned in 1663 by Boyle as being one then not generally known.

Gold chloride is largely used in photography for toning silver prints, a process which consists in the replacement of the silver by metallic gold.

Potassium Aurichloride, $KAuCl_4$.—When a strongly acid solution of gold chloride, to which the calculated quantity of potassium chloride has been added, is allowed to evaporate at a gentle heat, light-yellow monosymmetric needles having the composition $2KAuCl_4+H_2O$ are deposited. On the other hand, when the neutral or slightly acid solution is employed, large transparent rhombic tables of $KAuCl_4+2H_2O$ are formed, which easily effloresce on exposure. When heated these melt with evolution of chlorine, forming potassium aurous-chloride, $KAuCl_2$.

Sodium Aurichloride, $NaAuCl_4+2H_2O$, is obtained by dissolving common salt in a solution of gold chloride and concentrating the solution, when it is deposited in yellowish-red rhombic tables or prisms, which do not alter on exposure.

Ammonium Aurichloride, NH_4AuCl_4, appears to have been prepared by the alchemists, who employed aqua-regia containing sal-ammoniac for dissolving gold, and on cooling the solution obtained crystals which they considered to be a true gold vitriol. From the neutral solution large light-yellow rhombic tables of the composition $2NH_4AuCl_4+5H_2O$ separate. These are tolerably permanent. From an acid solution, on the other hand, the salt $4NH_4AuCl_4+5H_2O$, crystallises in monosymmetric plates. Both salts become anhydrous at 100°.

The chlorides of the calcium and magnesium groups, as well as those of manganese, nickel, cobalt, and thallium also form crystalline aurichlorides.

198 *Aurous Bromide*, AuBr, is formed as a greenish-yellow micaceous powder when auribromic acid, $HAuBr_4$, is heated at

115°, but is decomposed at a higher temperature. It is insoluble in water, and hydrobromic acid decomposes it into gold and the compound from which it has been obtained.

Auric Bromide, or *Gold Tribromide*, $AuBr_3$.—Finely-divided gold dissolves slowly in hydrobromic acid (Balard). In order to obtain the anhydrous compound, bromine is allowed to act upon gold powder, and the tribromide is extracted from the product by ether. When the solution is evaporated at a low temperature, the tribromide remains behind as a black crystalline crust, which dissolves slowly in water. The concentrated solution is viscid and almost black (Thomsen).

Auribromic Acid, $HAuBr_4+5H_2O$, is formed when bromine is allowed to act upon gold powder, and as soon as the reaction is over, a quantity of hydrobromic acid, having a specific gravity of 1·38, equivalent to the quantity of gold present, is added, and then bromine again added until the gold is completely dissolved. It crystallises in dark cinnabar-red flat needles, and melts at 77°.

Potassium Auribromide, $KAuBr_4+2H_2O$, is best prepared by adding bromine to powdered gold in presence of the requisite amount of potassium bromide. It forms reddish-purple monosymmetric crystals. Similar compounds of the other soluble bromides are also known.[1]

Aurous Iodide, AuI, is formed when hydriodic acid acts upon gold oxide:

$$Au_2O_3+6HI=2AuI+3H_2O+2I_2.$$

It is also formed when the neutral trichloride is precipitated by a solution of one molecule of potassium iodide, iodine being liberated. When finely-divided gold is boiled with hydriodic acid and a small quantity of nitric acid, and the filtrate allowed to run into hydriodic acid, a lemon-yellow coloured crystalline powder of aurous iodide is formed. It is when pure a very unstable white powder, which assumes a green colour when exposed to the air and deposits a bright surface of metallic gold on the inside of the vessel in which it stands. The decomposition takes place more quickly on warming, and at 120° it decomposes completely. Aqueous acid decomposes it only when heated.

Auric Iodide, AuI_3.—When a neutral solution of gold chloride is added to one of potassium iodide, the liquid becomes of a dark-green colour, and yields a green precipitate, which on

[1] Thorpe and Laurie, *Journ. Chem. Soc.* 1887, i. 576.

agitation dissolves again, inasmuch as potassium auriodide is formed. If, however, more gold solution is added, a permanent precipitate is formed, and this, after washing, may be dried, but it evolves iodine, and is converted on standing into aurous iodide. It forms dark-coloured crystalline auriodides with the soluble iodides, but it is doubtful whether the free acid exists.

Gold and Sulphur.

199 Gold does not combine directly with sulphur, but three sulphides corresponding in composition with the three oxides can be prepared indirectly. They are all dark-coloured powders which decompose into their elements when they are heated, and are soluble in the alkali sulphides.

Aurous Sulphide, Au_2S, is prepared by passing sulphuretted hydrogen into a solution of aurous cyanide in potassium cyanide and then acidifying. It forms a brownish-black powder which is soluble in water when it is freshly precipitated but loses this property when it is dried. It is not attacked by hydrochloric or sulphuric acids, but dissolves readily in potassium cyanide. This sulphide is also formed, mixed with gold and sulphur, when sulphuretted hydrogen is passed into a hot solution of auric chloride.[1]

Sodium Aurosulphide, $NaAuS + 4H_2O$, is obtained by heating metallic gold with sodium sulphide and sulphur, and treating the fused mass with water. The solution is filtered in an atmosphere of nitrogen and evaporated in a vacuum over sulphuric acid. Colourless, monosymmetric prisms are then deposited which soon become brown on exposure to air. The same salt is formed when aurous or auroauric sulphide is dissolved in sodium sulphide solution.[2]

That gold can be brought into solution by fusing it with liver of sulphur seems to have been known to Glauber, but Stahl, in his *Observationes Chymico-Physico-Medicæ*, is the first distinctly to mention this fact; and it may be added that he there explains that Moses burnt up the golden calf with alkali and sulphur, and gave the solution of liver of sulphur containing gold to the Israelites to drink.

Auro-auric Sulphide, AuS, is precipitated when sulphuretted

[1] Hoffmann and Krüss, *Ber.* 1887, **20**, 2369.
[2] Ditte, *Compt. Rend.* 1895, **120**, 320.

hydrogen is passed into a cold neutral solution of auric chloride, the sulphuretted hydrogen being partially oxidised to sulphuric acid :[1]

$$8AuCl_3 + 9H_2S + 4H_2O = 8AuS + 24HCl + H_2SO_4.$$

It is a black powder which dissolves in sodium sulphide solution and is thereby reduced to aurous sulphide, the liquid being found to contain sodium aurosulphide and sodium disulphide.[2]

It readily forms colloidal solutions in water and alcohol [3] and is dissolved by potassium cyanide. When left in contact with auric chloride it is reduced to metallic gold.[4]

Auric sulphide, Au_2S_3, is a very unstable substance and cannot be prepared by passing sulphuretted hydrogen into a solution of auric sulphide, nor by heating gold with sodium pentasulphide as stated by Berzelius. It is formed when anhydrous lithium aurichloride is treated with dry sulphuretted hydrogen at $-10°$.[5] It is an amorphous, graphitic powder, has the specific gravity 8·754 and decomposes into gold and sulphur at 200°. It is decomposed by the sulphides of ammonium but dissolves in sodium sulphide forming sodium aurisulphide. Like the other sulphides it is soluble in potassium cyanide.

200 *Sodium Aurous Sulphite*, $3Na_2SO_3 + Au_2SO_3 + 3H_2O$, is formed when acid sodium sulphite is added to a boiling alkaline solution of sodium aurate, or when this solution is saturated with sulphur dioxide at 50°. It is very easily oxidisable, but in presence of free sulphur dioxide the solution may be heated to boiling without decomposition occurring. When this solution is precipitated by alcohol the salt is obtained as a purple powder which appears yellow or green by reflected light. The corresponding ammonium salt, together with a compound of the formula $(NH_4)_2SO_3 + 3(NH_3Au)_2SO_3 + 3H_2O$, has also been described.

Potassium Auric Sulphite, $5K_2SO_3 + Au_2(SO_3)_3 + 5H_2O$, is formed when potassium sulphite solution is poured into a solution of potassium aurate, the above salt separating from the brown liquid in beautiful yellow needles. It is very unstable, and easily decomposes with separation of gold.

[1] Levol, *Ann. Chim. Phys.* 1850 (3), **30**, 355 ; Hoffmann and Krüss, *Ber.* 1887, **20**, 2074. [2] Ditte, *Compt. Rend.* 1895, **120**, 320.
[3] Schneider, *Ber.* 1891, **24**, 2241 ; 1892, **25**, 1164.
[4] Antony and Lucchesi, *Gazz.* 1889, **19**, 545.
[5] Antony and Lucchesi, *Gazz.* 1890, **20**, 601 ; 1891, **21**, ii. 209.

Sodium Auro-thiosulphate, $3Na_2S_2O_3 + Au_2S_2O_3 + 4H_2O$, is formed by the gradual addition of a neutral 2 per cent. gold solution to a solution containing three molecular proportions of sodium thiosulphate. It is necessary to wait after each addition until the red liquid which is formed becomes colourless. It is then precipitated with strong alcohol, and any common salt and sodium tetrathionate which may be present removed by repeated solution in water and precipitation with alcohol. The salt is formed according to the equation:

$$8Na_2S_2O_3 + 2AuCl_3 = 3Na_2S_2O_3 + Au_2S_2O_3 + 2Na_2S_4O_6 + 6NaCl.$$

It is also formed by the action of sodium thiosulphate on gold in the presence of oxygen. It crystallises in colourless needles, which have a sweet taste. Its solution is not reduced by ferrous sulphate or oxalic acid, nor is it at once decomposed by hydrochloric acid, or by dilute sulphuric acid, although this occurs on standing.

When barium chloride, and afterwards alcohol, are added to its solution a precipitate of the corresponding barium salt is obtained, from which a solution of the acid auro-thiosulphate, $3H_2S_2O_3 + Au_2S_2O_3$, is obtained by addition of the requisite quantity of sulphuric acid. This salt is not known in the anhydrous state, but the solution can be evaporated in the air to a syrupy consistency.

The above compounds do not exhibit the reactions either of the aurous salts or of the thiosulphates, and hence it is assumed that they contain a compound radical, whose hydrogen salt is the last-named compound. They may, therefore, be written as follows:

$$H_3S_4O_6Au.$$
$$Na_3S_4O_6Au + 2H_2O.$$

The extraction of gold from auriferous silver ores by means of sodium thiosulphate depends on the formation of these compounds.

Gold and Nitrogen and Phosphorus.

201 *Auro-diamine*, or *Fulminating Gold*, $Au(NH)NH_2$.—The preparation of this compound was first described with great accuracy in the *Last Testament* of Basil Valentine. He

obtained it by dissolving gold in *aqua-regia* mixed with *salarmoniac*, precipitating with *sal-tartari* (potashes), and subsequently washing with water. He then says: "Dry the gold-calx in the air where no sun shines, and especially not over the fire, for as soon as this powder is exposed to a little warmth it ignites and does a great deal of damage, for it then explodes with such great power and might that no man can withstand." He then describes its properties, and, amongst others, that it loses its explosive power when heated with sulphur. The name of fulminating gold (aurum fulminans) was given to it by Beguin in 1608. It was, however, also known under other names, and was used as a medicine. Angelus Sala, writing in the first half of the seventeenth century, mentions that no fulminating gold can be prepared if aqua-regia made with hydrochloric acid be employed instead of that made with sal-ammoniac, and Glauber says that the preparation obtained by means of volatile alkali (carbonate of ammonia) fulminates much more strongly than that made with *oleum tartari* (carbonate of potash). In spite of these observations but few chemists believed that the volatile alkali took part in the composition of the substance, and a great number of erroneous observations was made on the subject of the composition of fulminating gold.[1] Even Black in 1756 stated that the explosion was due to the sudden evolution of fixed air, although Kunkel, a very accurate observer, had already pointed out the true cause. For in his *Laboratorium Chymicum*, which appeared in 1716, fourteen years after his death, he described the preparation of fulminating gold, and discussed the various reactions which took place. He then continued: "Once I precipitated the gold with *oleum tartari*, distilled the menstruum to dryness, and then edulcorated; and I thus obtained a fine gold calx which became brown but did not fulminate at all; when, however, the same substance was imbibed several times with *spiritus urinæ* and very gently dried, it exploded violently." He also said that when this substauce was imbibed and afterwards distilled with oil of vitriol, an acid sal-volatile sublimed in the neck of the retort. "Hence," he added, "thou canst see whence the power in the *aurum fulminans* comes, namely from the *sal-volatile concentratum*." This view was confirmed by the experiments of Bergman and Scheele, who considered fulminating gold to be a compound of ammonia and gold calx. Hence the Lavoisierians termed this compound *oxide d'or ammoniacal*.

[1] Kopp, *Geschichte der Chimie*, **4**, 210.

The composition of this body was subsequently more exactly investigated by Dumas,[1] and later by Raschig.[2]

When ammonia is added to a solution of auric chloride, a mixture of fulminating gold with auric imidochloride, Au(NH)Cl, is precipitated and cannot be obtained quite free from chlorine even by prolonged digestion with ammonia. Pure fulminating gold is therefore best prepared by the action of concentrated ammonia on auric hydroxide. When dried over phosphorus pentoxide it has the composition $2AuN_2H_3+3H_2O$, and is a dirty olive-green powder which explodes most violently either on percussion or when heated. When it is boiled with water a portion of the nitrogen is evolved in the form of ammonia, and the powder becomes so unstable that it can scarcely be touched without undergoing decomposition. It is decomposed by hydrochloric acid with formation of auric chloride and ammonium chloride:

$$AuN_2H_3+5HCl=AuCl_3+2NH_4Cl.$$

With sulphuric acid, on the other hand, it appears to unite forming an extremely explosive sulphate, $(AuN_2H_3)_4H_2SO_4$. Both aurous and auroauric oxides are acted on by ammonia with formation of compounds analogous to fulminating gold. The aurous compound, *sesquiauramine*, has the formula $NAu_3.NH_3$, is not very explosive, and loses half its nitrogen when boiled with water, yielding *triauramine*, NAu_3. The derivative of auroauric oxide has the formula $N_2Au_3+5H_2O$, and is violently explosive.

Phosphides of Gold.—When gold is gently heated in phosphorus vapour, the compound Au_2P_3 is formed as a gray mass, which has the specific gravity 6·6, and easily loses phosphorus when more strongly heated. It is not attacked by hydrochloric acid but is decomposed by nitric acid, the phosphorus being dissolved and the gold left (Schrötter). A phosphide of the formula AuP is formed by the action of phosphuretted hydrogen on an ethereal solution of auric chloride.[3]

[1] *Ann. Chim. Phys.* 1855, **44**, 167.
[2] Raschig, *Annalen*, 1886, **235**, 341.
[3] Cavazzi, *Gazz.* 1885, **15**, 40.

Gold and Carbon.

202 *Aurous Cyanide*, AuCN.—This compound is obtained by the addition of hydrochloric acid to a solution of the potassium double salt and evaporation on the water-bath, the residue being washed in the dark. It is a fine yellow powder, showing iridescent colours, which consists of microscopic hexagonal tables insoluble in water, and in the dry state unalterable in the air. It is not attacked by the single acids, but dissolves readily in aqua-regia, as well as in ammonia, sulphide of ammonium, and sodium thiosulphate.

Potassium Auro-cyanide, $KAu(CN)_2$.—This compound, largely used in electro-gilding, is best obtained as follows: 7 parts of gold are dissolved in aqua-regia, precipitated by ammonia, the fulminating gold well washed and brought into a boiling solution of 6 parts of pure potassium cyanide. The solution is then filtered and allowed to cool, when, if it is not too dilute, the salt separates out in colourless rhombic pyramids having a pearly lustre. These have a saline and at the same time metallic taste, and are soluble in 7 parts of cold, and in rather less than half their weight of boiling water. The mother-liquor of these salts contains as impurity potassium chloride and potassium carbonate, and yields on evaporation impure crystals. These are, therefore, decomposed with hydrochloric acid as above described, and the resulting auro-cyanide dissolved in potassium cyanide.

Potassium auro-cyanide is also formed when finely-divided gold is treated in the presence of air with a solution of potassium cyanide [1] (p. 395):

$$4Au + 8KCN + O_2 + 2H_2O = 4AuK(CN)_2 + 4KOH.$$

Ammonium Auro-cyanide, $NH_4Au(CN)_2$, is obtained by mixing a solution of the foregoing salt with one of ammonium sulphate, and removing the potassium sulphate by precipitation with alcohol. The crystals have a disagreeable metallic taste and are easily soluble in water, alcohol, and ether.

Auric Cyanide, $Au(CN)_3$, is not certainly known in the free state, but exists in combination with hydrocyanic acid and other cyanides.[2]

[1] Elsner, *J. Pr. Chem.* 1846, **37**, 333; Johnston, *Phil. Mag.* 1836 [3], **9**, 266.

[2] Himly, *Annalen*, 1842, **42**, 340; and Gmelin, *Handbook*, **8**, 41.

Auricyanic Acid, $2HAu(CN)_4 + 3H_2O$, is obtained from the potassium salt by precipitation with silver nitrate. The precipitated silver salt is washed with cold water and decomposed by somewhat less than the requisite quantity of hydrochloric acid. The filtrate yields on evaporation tabular crystals which are easily soluble in water, alcohol and ether.

Potassium Auricyanide, $2KAu(CN)_4 + 3H_2O$, is obtained by mixing hot concentrated solutions of gold chloride and potassium cyanide. On cooling it crystallises in large colourless efflorescent tablets. It is used for electro-gilding.

Ammonium Auricyanide, $NH_4Au(CN)_4 + 2H_2O$, is formed when auric hydroxide is dissolved in ammonium cyanide. It forms either four or six-sided tablets which are easily soluble in water and alcohol but not in ether.

Aurous Thiocyanate is only known in combination with other thiocyanates. *Potassium auro-thiocyanate*, AuSCN + KSCN, is obtained with evolution of thiocyanic acid, when a neutral gold solution is poured into a hot solution of potassium thiocyanate. It crystallises in yellow obtuse prisms. When hydrochloric acid is added to the solution copper-red needles separate out, and silver nitrate precipitates the *double silver gold thiocyanate*, AuSCN + AgSCN. Ammonia also produces a white precipitate of *aurammonium thiocyanate* $(AuNH_3)SCN$.

Auric Thiocyanate is not known in the free state, but if a solution of gold chloride be precipitated by potassium thiocyanate in the cold, an orange yellow precipitate of $KAu(SCN)_4$ is thrown down, which crystallises in slender needles and is partially decomposed by hot water.

Detection and Estimation of Gold.

203 When a gold compound is heated on a carbonised match in the reduction flame, a yellow malleable bead is obtained which dissolves in aqua-regia. If this solution be dropped on to filter paper and one drop of stannous chloride added, a purple red colour is observed. Gold can be readily detected in its solutions inasmuch as it is obtained in the metallic state by reducing agents, the well-washed precipitate being dissolved and the solution tested with stannous chloride. This is best done by pouring the boiling solution which is supposed to contain gold into a small quantity of concentrated stannous chloride

solution. If gold be present, the precipitated stannous hydrate has a purplish colour. One part of gold in 100,000,000 of water can thus be detected.[1]

In the ordinary method of analysis gold is precipitated along with tin, antimony, arsenic and platinum. The method adopted for its separation is described under the last of these.

The spark spectrum of gold has been mapped by Kirchhoff, Thalén, Huggins and Krüss. The brighest lines are 6,278, 5,957, 5,656 and 5,838 in the orange and yellow, and 5,230 and 4,792 in the green and blue; there are also several lines in the violet and ultra violet. Gold compounds do not impart any tint to the non-luminous gas flame.

Assay of Gold Ores and Bullion.—The amount of gold contained in an ore is usually ascertained by fusing the ore with red-lead or litharge, charcoal, sodium carbonate and a little metallic iron. In this way a button of lead is obtained which contains all the gold and silver of the ore. This button is then cupelled, the residual bead of gold treated with nitric acid and the pure gold which remains weighed. In order to determine the value of gold bullion it is cupelled with lead with addition of so much silver that the quantity of the latter is about two and a half times that of the gold present. A gold-silver alloy is thus obtained which is rolled into foil and then boiled with nitric acid of specific gravity 1·26. The residual gold cornet having been well washed is placed in a small crucible and heated in a muffle to a point just below that at which gold melts, in order to render it coherent, after which it is cooled and weighed.

The assaying of gold is an operation of much importance and one in which great accuracy is needed. The errors attaching to the process are chiefly (1) errors in weighing, (2) loss of gold by absorption in the cupel and by volatilisation, (3) slight solution of the gold by the acid, (4) and most important, the presence of a portion of silver in the gold cornet, together with occluded gases. In order to compensate for these various errors, an allowance, called the *surcharge*, is made on each assay, the value of this allowance being determined by special experiments with known amounts of pure gold. In this way and by carrying out all the processes with unvarying uniformity, as well as by making the assay on a number of samples placed in different parts of the muffle, very great accuracy can be attained. The Bank of England carry on their enormous transactions in bullion

[1] Rose, *Chem. News*, 1892, **66**, 271.

upon triple assays of each ingot made by some scientific assayer of high standing, and in every mint two or more assayers are employed to check each other's results. When every precaution is taken the limit of accuracy which can be obtained with high standard alloys appears to be one part in 50,000.[1]

The *atomic weight of gold* was first determined with accuracy by Berzelius,[2] who ascertained the quantity of mercury necessary to precipitate gold from its chloride, and obtained as the mean of two experiments the number 195·7 (O = 15·88). At a later period[3] he determined the relation between gold and potassium chloride in potassium aurichloride, $KAuCl_4$, and obtained the number 195·2, whilst Levol[4] found the number 194·8 by reducing a solution of pure auric chloride with sulphur dioxide and determining the relation between the precipitated gold and the sulphuric acid which was formed.

The atomic weight has more recently been determined by Thorpe and Laurie, Krüss, and Mallet. The first-named chemists[5] started with potassium auribromide which was carefully heated to convert it into metallic gold and potassium bromide. The relation of gold to potassium bromide in this mixture was then determined as well as the amount of silver necessary to precipitate the potassium bromide corresponding to a known amount of gold, and the amount of silver bromide thus formed. The mean result of these experiments was 195·86 (O = 15·88). Krüss[6] arrived at a somewhat lower number, 195·65, by the analysis of weighed amounts of the same salt. Mallet[7] finally obtained the number 195·77, intermediate between those of Thorpe and Laurie, and Krüss by the analysis of auric chloride, auric bromide and potassium auribromide. Other determinations by somewhat less reliable methods yielded him rather higher numbers. The atomic weight may therefore be taken as 195·7.

[1] Rose, *Journ. Chem. Soc.* 1893, i. 700.
[2] *Schweigg. Journ.* **7**, 44.
[3] *Berz. Jahresber.* **25**, 41.
[4] *Ann. Chim. Phys.* 1850 (3), **30**, 355.
[5] *Journ. Chem. Soc.* 1887, i. 866.
[6] *Ber.* 1887, **20**, 207; *Annalen*, 1887, **238**, 30, 242.
[7] *Proc. Roy. Soc.* 1890, **46**, 71.

GROUP II.

Sub-Group (*a*).—The Alkaline Earth Metals :—

Calcium.
Strontium.
Barium.

Sub-Group (*b*).—The Magnesium Group of Metals :—

Beryllium.
Magnesium.
Zinc.
Cadmium.
Mercury.

204 The metals of this group are divalent in almost all their compounds, the only important exception being the element having the highest atomic weight, viz., mercury, which in addition to the divalent derivatives forms a series of salts in which the metal is probably monovalent. The remaining metals only form one basic oxide which has the general formula $M''O$, and these also yield the corresponding hydroxide $M''(OH)_2$, which in the case of the metals of sub-group (*a*) is soluble and in that of the sub-group (*b*) almost insoluble in water. All of these elements combine directly with oxygen fairly readily forming the divalent oxide.

In the table given on pp. 46, 47, it will be seen that beryllium occurs in the same sub-group as calcium, strontium and barium ; in its general properties, however, it is more closely allied with magnesium and zinc, and is therefore described together with these metals.

THE ALKALINE EARTH METALS.

205 The name earth was used by the older chemists to designate all those non-metallic substances which were insoluble in water and did not undergo alteration when exposed to a high temperature. It was afterwards observed that some of these,

such as lime and magnesia, were closely allied to the alkalis, inasmuch as they possessed an alkaline reaction and neutralised acids. These bodies were therefore termed *terræ alcalinæ*, and this name was subsequently also applied to baryta and strontia. As the other compounds of magnesium resemble the corresponding ones of zinc, cadmium and beryllium more nearly than those of barium, strontium and calcium, this metal is now no longer regarded as belonging to this group, the term metals of the alkaline earths being therefore confined to the metals contained in the oxides, lime, strontia and baryta.

The alkaline earths, like the alkalis, were supposed to be elementary bodies until Davy, in the year 1807, showed that each earth was a compound of a metal and oxygen.

The metals themselves, which have only been obtained in small quantity, very readily oxidise in moist air and decompose water at the ordinary temperature with evolution of hydrogen and formation of the hydroxide. The oxides only fuse at the temperature of the electrical furnace, and combine with moisture with great avidity forming the hydroxides, the solubility of which in water increases with the atomic weight of the metal. They also form peroxides having the formula $M''O_2$, that of barium being obtained by the direct union of barium monoxide and oxygen. The salts for the most part crystallise well; the carbonates, phosphates and sulphates are either very sparingly soluble or insoluble in water, as are also their salts with many organic acids.

CALCIUM Ca = 39·7.

206 The very early application of mortar to building purposes shows that the ancients were well acquainted with the properties of lime and its preparation by the burning of limestone. In the writings of Dioscorides and Pliny we find a description given of the process of lime-burning, as well as of that of slaking lime.

Calcium occurs very largely diffused in nature, especially as the carbonate, which occurs in various forms, such as calc-spar, arragonite, chalk, marble, limestone, coral, &c. United with carbonate of magnesia, as magnesian limestone or dolomite, it forms whole mountain ranges, and this compound, when crystal-

lised, is known as bitter-spar. Many other minerals contain calcium carbonate in isomorphous mixtures; amongst these may be mentioned chalybite or brown-spar (CaMgFeMn) CO_3; mangano-calcite (MnCaMg)CO_3; plumbocalcite (CaPb)CO_3, &c. Calcium also occurs in large quantity as sulphate, either as the anhydrous compound, termed anhydrite, $CaSO_4$, or in the hydrated form, as selenite or gypsum, $CaSO_4 + 2H_2O$. Calcium phosphate, combined with calcium chloride or calcium fluoride, occurs in the well-known minerals, apatite and osteolite. Calcium borate is also found in nature combined with many other metallic borates, whilst silicate of calcium occurs as an almost invariable constituent of all silicates. The solid constituents found in river and spring waters also consist mainly of calcium carbonate or calcium sulphate, and these, as well as phosphate and fluoride of calcium, are found in sea-water. Calcium salts form a never-failing component of the bodies of plants and animals, and cannot be replaced by any other salts. They accumulate in the leaves of plants; the roots and seeds, as a rule, yield only small quantities of them. The bones and teeth of animals contain large amounts of calcium phosphate, together with some carbonate and fluoride. Egg shells and the shells of mollusca, on the other hand, chiefly contain calcium carbonate. Calcium also occurs in the sun, in meteorites, and in certain of the fixed stars.

Preparation of Metallic Calcium.—Calcium was first prepared by Davy by the electrolysis of calcium chloride in the presence of mercury, the calcium remaining as a metallic powder upon heating the amalgam thus obtained. It was first obtained in a coherent metallic mass by Matthiessen[1] in 1856. A mixture in the proportion of two molecules of calcium chloride to one molecule of strontium chloride, with a small quantity of sal-ammoniac, which mixture is more fusible than calcium chloride alone, is melted in a small porcelain crucible in which a carbon positive pole is placed, while a thin harpsichord wire wound round a thicker wire, and dipping only just below the surface of the melted salt, forms the negative pole. The metal calcium is then reduced in beads, which hang on to the fine wire, and may be obtained by withdrawing the negative pole every two or three minutes, together with the small quantity of crust which is attached to it. Calcium may also be obtained by the modification of the above process described under strontium. Frei

[1] *Journ. Chem. Soc.* 1856, 28.

obtained it, by the electrolysis of the chloride, in globules weighing from 2·4 to 4 grams. Another way of obtaining the metal is to fuse a mixture of one part of sodium with seven parts of fused iodide of calcium in a closed iron crucible. The temperature is first raised to a dull red-heat, and afterwards to a bright red-heat.[1] Another process is to fuse three parts of calcium chloride with four parts of zinc and one part of sodium. In this way an alloy of zinc and calcium is produced, which is then heated in a crucible made of gas carbon until the zinc volatilises, when the fused calcium is found in the form of a button (Caron).[2]

Calcium is a yellow metal, which gives a yellow streak on touch-stone. It is harder than lead, is tenacious and malleable, and has a specific gravity of 1·5778 (Bunsen and Matthiessen). According to Frei it has the colour of aluminium, and is very brittle.[3] It may be preserved in perfectly dry air for many days without undergoing oxidation; in moist air it is readily oxidised. When heated to redness in the air, it burns with a very bright yellow light, and when thrown into water decomposes it with violent evolution of hydrogen.

COMPOUNDS OF CALCIUM.

Calcium and Oxygen.

207 *Calcium Monoxide* or *Lime*, CaO, is formed in the pure state by the ignition of the pure carbonate, as Iceland-, or calc-spar, or white marble, in a crucible in a current of indifferent gas; otherwise the decomposition is not complete (p. 110).

On the large scale lime is burnt in kilns, the interiors of which are usually egg-shaped. The limestone is mixed up with coal or other combustible matter, one bushel of coal generally sufficing to make five or six bushels of lime. In some cases an arch is formed over the fire-grate with lumps of limestone, the kiln filled up with smaller pieces, a fire kindled below the arch, and this kept up for thirty-six to forty-eight hours. The kiln is then allowed to cool, the lime removed, and a fresh charge introduced. An improved and continuous process of

[1] Liés Bodart, and Jobin, *Ann. Chim. Phys.* 1858 [3], **54**, 364.
[2] *Annalen*, 1860, **115**, 355.
[3] *Annalen*, 1876, **183**, 367.

lime burning is now often employed in which the charge of limestone and coal is added from time to time at the upper part of the kiln, and the quicklime withdrawn at the lower part. A great saving of fuel is thus effected, and the smoke which is always given off from the common kiln is, in the improved kiln, drawn into a high chimney and completely burnt.

Pure lime is a white amorphous mass, having a specific gravity of 3·08; it does not fuse at the temperature of the oxy-hydrogen flame, but may be melted in an electrical furnace and solidifies on cooling to a confusedly crystalline mass. At a temperature rather below its melting point it rapidly becomes crystalline.[1] It is also obtained crystallised in cubes by heating calcium nitrate in a porcelain flask.[2] On exposure to the air it combines with moisture passing into the hydroxide $Ca(OH)_2$, which then absorbs carbon dioxide. When water is poured on to quicklime the latter is converted into the hydroxide with great evolution of heat, the temperature rising in some cases as high as 150°. The evolution of heat may be well shown by strewing a few grains of gunpowder on to the lime, whilst it is being slaked, when the powder will take fire. Although lime unites so readily with water it is in absence of this a very inert substance; thus it does not combine to an appreciable extent with dry chlorine, carbon dioxide, sulphur dioxide and oxides of nitrogen below 300-350°, whereas it is readily acted on by these substances in presence of moisture.[3]

The most important use of lime is in the preparation of mortars and cements for building purposes (p. 445), and its value for these purposes depends upon the nature of the limestone from which it has been prepared. The lime obtained from pure limestone slakes readily and is termed a "fat" lime, but if the limestone contains magnesia it only forms a thin mixture with water, and is termed a "poor" lime. When the quantity of magnesia rises to 25-30 per cent. the product is almost useless for building purposes. If the limestone used contains silica in considerable quantity the resulting lime yields a mortar which hardens under water and is known as hydraulic lime, and the mortar obtained from it as hydraulic mortar (p. 445). The presence of clay in the limestone frequently causes it to vitrify if too strongly heated, a hard crust of silicates being formed on

[1] Moissan, *Compt. Rend.* 1892, **115**, 1034.
[2] Brügelmann, *Wied. Ann.* 1877, **2**, 466.
[3] Veley, *Journ. Chem. Soc.* 1893, i. 821; 1894, i. 1.

the surface which causes it to slake very slowly. Such lime is said to be "dead burnt."

In addition to its use for building purposes lime is used for the purposes of drying gases and liquids, and in numerous analytical processes, and also, when slaked, for the purification of coal-gas (vol. i. p. 779) and manufacture of bleaching powder.

Calcium Hydroxide, $Ca(OH)_2$.—This substance, also known as *slaked lime*, is obtained, as already stated, by the action of water on quicklime. It is a white impalpable powder, having a specific gravity of 2·078 (Filhol). Calcium hydroxide is likewise obtained as a white precipitate, when a solution of caustic potash or soda is added to a tolerably strong solution of calcium chloride. If a very strong or saturated solution of calcium chloride be employed in the above experiment, the whole mass becomes solid. This fact was observed in 1686 by Francisco Lana, and described by him as the "chemical miracle." Calcium hydroxide dissolves more readily in cold than in hot water; 100 parts of water at 15°·6 dissolve 0·1368 parts, and at 100° 0·0752 parts (Wittstein). The clear solution, evaporated in a vacuum over sulphuric acid, deposits the hydroxide either in the form of small tables or of small prismatic crystals.

The solution of calcium hydroxide, usually known as lime-water, possesses an alkaline reaction and taste. It quickly absorbs carbon dioxide from the air, and is used in medicine and in the laboratory. As the ordinary slaked lime often contains small quantities of baryta and strontia together with soluble salts of the alkalis, it is usual to treat the powder several times with water, and only to employ the last solution.

Milk of Lime is calcium hydroxide suspended in water.

Calcium Dioxide, CaO_2, was discovered by Thénard, who obtained it by precipitating lime-water with hydrogen dioxide. In order to procure the substance in the pure state the hydrogen dioxide must be added in excess to lime-water. The precipitate possesses the composition $CaO_2 + 8H_2O$, and consists of microscopic quadratic tables or prisms, which are sparingly soluble in water and insoluble in alcohol.[1] On exposure to the air the crystals effloresce, and when heated to 130° they lose their water leaving behind a light powder of the anhydrous oxide. When further heated the substance loses half its oxygen without fusing.

[1] *Ann. Chim. Phys.* 1818, **8**, 313.

Calcium and the Halogens.

208 *Calcium Fluoride*, CaF_2, occurs as the mineral known as fluor-spar, which has from early times been used in the fluxing of ores, whence its name is derived. Agricola says: "Fluores lapides gemmarum similes sed minus duri, qui ignis calore liquescunt;" and then further: "Dum metalla excoquuntur, adhibere solent, reddunt enim materiam in igne non paulo fluidiorem."

Fluor-spar occurs largely in Derbyshire in veins, especially in the celebrated limestone caves in the Castleton valley. It is there found as a coloured variety which is commonly known as *Blue John*, and one of these large caverns is termed the Blue John cave. It is also found in Saxony and in many other countries. It crystallises in cubes and

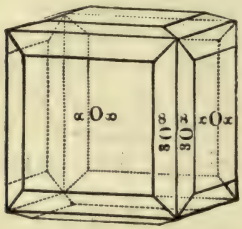


Fig. 89.

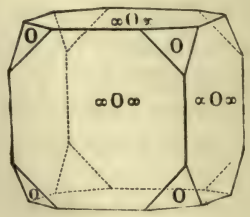


Fig. 90.

octohedra, and in combinations of these two forms, or in other forms belonging to the regular system (Figs. 89, 90). In the pure condition it is colourless; in general, however, it has a blue, violet, red, green, yellow, or brown colour. Those samples which have a bright colour are worked up into vases, dishes, cups, &c. Calcium fluoride also occurs in small quantity in the ashes of certain plants, in bones, in the enamel of the teeth, in sea-water and in the water of certain mineral springs. It is very nearly insoluble in water and dilute acids.

When precipitated calcium fluoride, obtained by mixing a solution of calcium chloride with one of a soluble metallic fluoride, is heated with water slightly acidified with hydrochloric acid, the precipitate is found to consist of microscopic octohedra.

The property which fluor-spar possesses of becoming luminous when heated, giving rise to the term fluorescence, was first mentioned by Elsholz in 1677, and further described by Leibnitz in 1710.

Calcium Chloride, $CaCl_2$.—Isaac Hollandus in the fourteenth century describes, under the name of *sal-ammoniacum fixum*, a substance which he obtained by heating together sal-ammoniac and lime. Homberg in 1693 noticed that this salt, when fused, became phosphorescent, and hence it was long known as Homberg's phosphorus. Calcium chloride is found in solution in sea-water, and in many mineral springs. It likewise occurs as a constituent of a few minerals, such as tachhydrite, $CaCl_2 + MgCl_2 + 12H_2O$, and apatite $3Ca_3(PO_4)_2 + (CaCl_2CaF_2)$.

In order to prepare pure chloride of calcium, Iceland spar, chalk or white marble is dissolved in hydrochloric acid until the latter is nearly saturated. Chlorine water is then added, in order to oxidise any iron or manganese compounds which may be present. These impurities are next precipitated by the addition of milk of lime, and the precipitate is filtered off. The slightly alkaline solution is then acidified with hydrochloric acid, and the solution evaporated either to the point of crystallisation or to dryness. Chloride of calcium is obtained on the large scale as a bye-product in several manufacturing processes, as in that of potassium chlorate, in the ammonia-soda process, the Weldon chlorine process, &c.

The hydrated salt crystallises from a saturated solution in large hexagonal prisms, which have the composition $CaCl_2 + 6H_2O$. These melt at 30·2°, and deliquesce rapidly in the air, forming a thick liquid, to which the name of *oleum calcis* was formerly given. The crystals dissolve in water, producing a considerable diminution of temperature; and if $1\frac{1}{3}$ parts of the crystallised salt be mixed with 1 part of snow the temperature sinks to −48°. Heated to 200° this hydrate loses four molecules of water, and a white porous hygroscopic mass remains behind, which is largely used as a means of drying gases and organic liquids. If this hydrate is heated more strongly, the anhydrous salt is obtained. This last melts at about 725°, and solidifies on cooling to a crystalline mass, which has a specific gravity of 2·205, and is also used as a desiccating agent.

When a solution of 103–127 parts of calcium chloride in 100 parts of water is cooled to 18—38°, a hydrate of the formula $CaCl_2 + 4H_2O$ separates out; it exists in two modifications, the more stable compound being less soluble in water than the other. The stable modification passes into the dihydrate,

$CaCl_2 + 2H_2O$, at 45·3°, and the labile modification into the same hydrate at 38·4°; at 175·5° the monohydrate separates from the solution, and at 260° this is replaced by the anhydrous salt.[1]

100 parts of water dissolve

at	0°	10°	20°	30°	40°	50°	70°	90°	99°
	49·6	60	74	93	110	120	136	147	154

parts of $CaCl_2$ (Mulder). Calcium chloride is also very readily soluble in alcohol.

A solution of 50 parts of the anhydrous salt in 100 parts of water boils at 112°, one containing 200 parts boils at 158°, and one containing 325 parts boils at 180°. Such solutions are employed as baths for constant temperatures above 100°.

Calcium chloride absorbs dry ammonia, giving rise to a voluminous powder having the composition $CaCl_2 + 8NH_3$, which on exposure to the air, on solution in water, or on heating, loses ammonia, and which takes fire when thrown into chlorine gas.

If chloride of calcium solution be boiled with slaked lime and the solution filtered hot, a basic salt separates out on cooling in long white needle-shaped crystals, having the composition $ClCa{\cdot}O{\cdot}Ca(OH) + 7H_2O$, which is known as *calcium oxychloride.*

Calcium Bromide, $CaBr_2$, and *Calcium Iodide*, CaI_2, are salts very similar in their properties to calcium chloride.

209 *Chloride of Lime, or Bleaching Powder.*—This well-known bleaching agent and disinfectant is obtained by the action of chlorine on slaked lime, and appears to have been first prepared by Charles Tennant, at the St. Rollox works, Glasgow, in 1799. Berthollet had some years previously suggested the use of chlorine as a bleaching agent, and in 1789 a bleaching liquor was manufactured by the action of chlorine on a solution of caustic potash, and sold under the name of "Eau de Javelles." Tennant in 1798 replaced the expensive potash by milk of lime, thus obtaining a bleaching liquor, but it was only in the following year that he substituted slaked lime for milk of lime and obtained the dry powder.

The action of chlorine on milk of lime is analogous to its action on potash, a solution of calcium hypochlorite and chloride being obtained:—

$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(ClO)_2 + 2H_2O,$$

[1] Roozeboom, *Zeit. Phys. Chem.* 1889, **4**, 31.

and it was supposed by Balard in 1834 that the solid powder was also a mixture of chloride and hypochlorite, his views being for some time generally accepted. It was, however, pointed out by Fresenius[1] that a substance containing so much calcium chloride must be far more hygroscopic than bleaching powder is found to be, and a number of other constitutional formulæ were proposed, the most important being those of Stahlschmidt[2] and Odling.[3]

According to Stahlschmidt's supposition the action of chlorine on slaked lime takes place in the following manner:—

$$3Ca(OH)_2 + 2Cl_2 = 2Ca\begin{<}Cl\\OH\end{>} + CaCl_2 + 2H_2O.$$

On addition of water the calcium chloride dissolves and the basic hypochlorite decomposes into hypochlorite and free lime:—

$$2Ca\begin{<}Cl\\OH\end{>} = Ca(OH)_2 + Ca(OCl)_2.$$

According to Odling's formula the calcium is combined with the negative radicals of both hydrochloric and hypochlorous acid as shown by the formula $Ca\begin{<}Cl\\OCl\end{>},H_2O$, and this compound by the action of water is resolved into calcium chloride and hypochlorite:—

$$2Ca\begin{<}Cl\\OCl\end{>} = CaCl_2 + Ca(ClO)_2.$$

The subject has been carefully investigated by Lunge in conjunction with Schaeppi and Naef,[4] and the results of their investigations have shown that the latter view is probably the correct one. By careful preparation it is possible to obtain a powder containing 44 per cent. of available chlorine (*i.e.* chlorine which on addition of water yields hypochlorous acid), whilst according to Stahlschmidt's formula the maximum quantity of available chlorine is only 39 per cent. Further, no calcium

[1] *Annalen*, 1861, **118**, 317. [2] *Dingl. Polyt. Journ.* 1876, **220**, 243.
[3] *Manual of Chemistry*, **1**, 56.
[4] *Dingl. Polyt. Journ.* **237**, 63; *Annalen*, 1883, **219**, 129; 1884, **223**, 106.

chloride can be extracted from bleaching powder by means of alcohol, and the whole of the chlorine may be expelled by the action of carbon dioxide, which could scarcely be the case if it contained calcium chloride. O'Shea[1] has also shown that for every molecule of CaO, two atoms of chlorine can be added, and that of this chlorine half is available for the formation of hypochlorous acid, which further confirms Odling's formula. Dreyfuss[2] has raised objections to this formula, but his conclusions have been shown by Lunge and Schoch to be untenable.[3]

Manufacture of Bleaching Powder.—Bleaching powder is obtained on a very large scale in the alkali works from the hydrochloric acid evolved in the production of salt-cake. For the purpose of evolving the chlorine required for the manufacture large stills are employed, shown in Figs. 91 and 92. These are made of Yorkshire flag soaked in tar, the joints being rendered tight by india-rubber rope on which the stone rests, as shown in Fig. 91. The material now usually employed for the generation of chlorine from hydrochloric acid, is the manganese dioxide, obtained by precipitation in what is known as Weldon's process. (A) is the tap for admitting the hydrochloric acid; (B) is the inlet to admit the finely divided precipitated manganese mud; (C) the lute and pipe to carry off the chlorine; (D) a pipe made of ebonite through which steam is led for the purpose of heating the mixture. Fig. 92 shows the plan of the same chlorine-still.

The chlorine gas passes from the still into large chambers of which Fig. 93 shows the elevation and end-section, and Fig. 94 the corresponding plan. These chambers are sometimes made of lead, sometimes of Yorkshire flag, and sometimes of iron plate covered with asphalt varnish. They are generally sixty feet long, eighteen feet wide, and seven feet in height. Dry slaked lime is filled into the chamber in such quantity that a layer of from four to five inches covers the bottom. The whole is ridged with a rake made for the purpose, the apex of each ridge being from five to six inches, and the bottom of the furrow from two-and-a-half to three inches above the floor. The chlorine is delivered through the pipe and lute (E). A considerable distance is generally allowed between the chlorine-still and the chamber in order to permit of the condensation of moisture and the cooling of the gas. (F) is the exit pipe con-

[1] *Journ. Chem. Soc.* 1883, i. 410. [2] *Bull. Soc. Chim.* 1885 (2), **41**, 600.
[3] *Ber.* 1887, **20**, 1474.

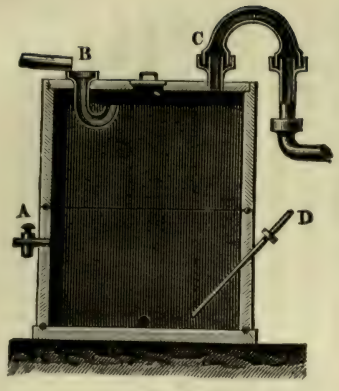


FIG. 91.

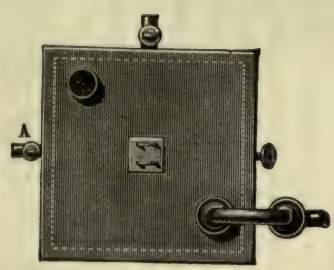


FIG. 92.

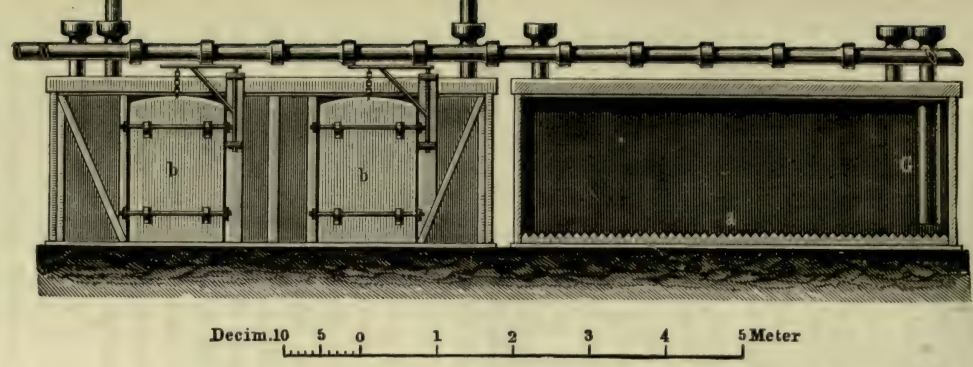


FIG. 93.

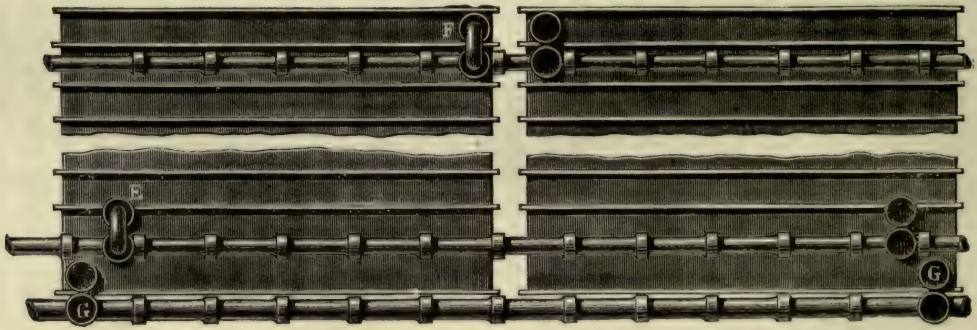


FIG. 94.

nected with a fresh lime chamber for the absorption of the surplus chlorine. (G) is an exhaust pipe for drawing off the last remaining quantities of the unabsorbed chlorine when the operation is complete. The exterior view, Fig. 93, shows the doors and bolts and the gallows for the swinging of the doors. The section shows the lime lying on the bottom of the chambers, whilst the arrangement of the pipes and lutes is seen in Fig. 94. In these chambers the absorption of chlorine occupies about six days. After the lime has been placed upon the floor of the chamber, chlorine is turned on until the chamber is full, as seen by windows placed at each end, the air and any surplus chlorine escaping from the chamber and passing by the circulating pipes into the next or some other chamber where there is more fresh lime. The air which is displaced from this, escapes either into the atmosphere directly or into a third chamber. When the first chamber has been filled with chlorine it is allowed to stand for about two days, during which time the gas is completely or nearly completely absorbed, and the lime is then found to contain from 25 to 30 per cent. of available chlorine. Any unabsorbed gas is then drawn off by means of the exit pipe (G), the doors are opened, and workmen enter and turn the lime. After turning, the doors are closed, and more chlorine is admitted, the quantity being sufficient to raise the amount of chlorine after absorption for a second period of two days to from 36 to 37 per cent. The unabsorbed chlorine is then drawn off as before, and the powder packed and sent to market. Occasionally a third treatment is necessary, but this rarely occurs except in hot weather, when the absorption of the chlorine takes place more slowly than usual.

In the old process of manufacture, when native manganese was always employed, from 90 to 100 parts of the ore, containing 60 per cent. of the dioxide, yielded 100 parts of bleaching powder containing 35 per cent. of available chlorine. By Weldon's process nearly all the manganese dioxide can be regained from the residual chloride of manganese, and is employed again for the evolution of chlorine. A certain loss, however, takes place, and from 5 to 8 per cent. of native manganese ore containing 60 per cent. of MnO_2 has to be added together with the regenerated manganese dioxide in order to produce 100 parts of bleaching powder of 35 per cent. strength. The quantity of hydrochloric acid employed for the production of one ton of bleaching powder varies in different works according to the care

with which the process is carried on. The usual practice is to make one ton of bleaching powder from the acid evolved by the decomposition of three-and-a-half tons of salt. Some manufacturers, however, use considerably less than this, and Weldon believes that the acid obtained from two tons of salt is sufficient for the purpose. In practice it is found that 11 cwt. of caustic lime are required to form one ton of bleaching powder.

An improved form of bleaching powder chamber has been invented by Deacon for the manufacture of bleaching powder according to his patented process. The principles of this process have already been referred to (vol. i. p. 157), chlorine being obtained directly from the gaseous hydrochloric acid of the salt-cake furnace without the employment of oxide of manganese. In this process considerable quantities of nitrogen pass into the chamber together with the chlorine, so that it is necessary that a graduated system of absorption should be carried out; the lime which is nearly saturated with chlorine, being exposed to the strongest gas whilst the last traces of chlorine are extracted by layers of comparatively fresh lime. These chambers are shown in elevation and section in Figs. 95 and 96. Chlorine gas mixed with nitrogen passes in through the tube (A), being drawn over the lime by means of exhausters. Each chamber or block is divided by vertical walls into fourteen squares; each section contains nineteen shelves 20 feet long by 4 feet wide, and the lime is spread on these to the depth of about five-eighths of an inch. Part of the elevation shows the doors, which form the sides of the chamber, in position; the other part shows the arrangement of the shelves seen when the doors are down. The end section shows the mode in which the shelves are arranged, and the way in which the chlorine is divided into streams during its passage through the lime. When the lime in one chamber has come up to strength, small plates on each shelf are removed from the top, and the bleaching powder simply falls into a barrel placed on a tram-car beneath, and in this way the product is easily packed.

During recent years several forms of continuous mechanical apparatus have been successfully adopted, in which the slaked lime is transported in a continuous stream by single or double conveyors in an opposite direction to the stream of chlorine, the finished bleaching powder being delivered direct into casks, thus avoiding the disagreeable task of hand packing.[1]

[1] Mond, *Nature*, 1896, **54**, 477.

The following complete analyses by Pattinson show the exact composition of good samples of commercial chloride of lime. The first two were manufactured from lime obtained from two different kinds of Irish limestone, and the third from lime from a French source :—

	A.	B.	C.
Available chlorine	37·00	38·30	36·00
Chlorine as chloride	0·35	0·59	0·32
Chlorine as chlorate	0·25	0·08	0·26
Lime	44·49	43·34	44·66
Magnesia	0·40	0·31	0·43
Ferric oxide	0·05	0·04	0·02
Alumina	0·43	0·41	0·33
Manganous oxide	trace	trace	trace
Carbon dioxide	0·18	0·30	0·48
Siliceous matter	0·40	0·30	0·50
Water and loss	16·45	16·33	17·00
	100·00	100·00	100·00

210 *Properties of Bleaching Powder.*—Commercial bleaching powder contains about 20–35 per cent. of available chlorine, and forms a homogeneous white powder, which gradually becomes moist on exposure to the air, and also absorbs carbon dioxide with evolution of hypochlorous acid, to which it owes its characteristic smell. It invariably contains free lime, and although by repeated powdering and fresh treatment with chlorine this may be reduced to a very small quantity, the reaction can never be made complete. When preserved in closed vessels, it undergoes decomposition under circumstances which are at present undetermined, and this decomposition is sometimes so sudden and the rise of temperature so great that explosions occasionally occur. When mixed with a small quantity of water it forms a creamy liquid, and dissolves in 20 parts of water leaving a slight residue, the solution containing as already stated a mixture of calcium chloride and hypochlorite. On boiling the solution oxygen is evolved and only a small quantity of calcium chlorate formed, and on boiling with sodium hydrogen carbonate it gives off carbon dioxide and oxygen, the hypochlorous acid which is first formed, decomposing into hydrochloric acid and oxygen, and the former then decomposing the carbonate with evolution of carbon dioxide. When the concentrated aqueous solution is allowed to evaporate over

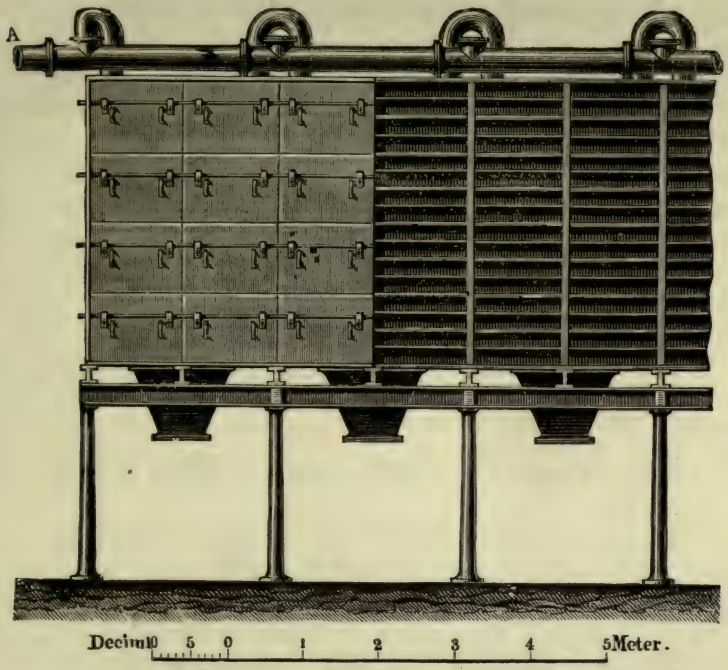


FIG. 95.

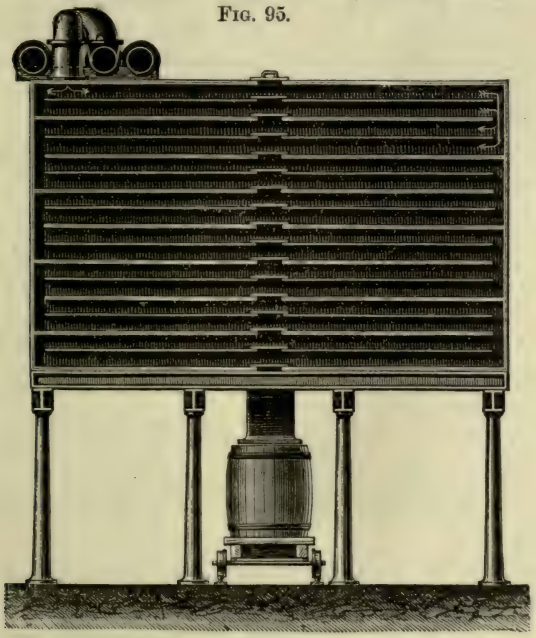


FIG. 96.

sulphuric acid, crystals of calcium hypochlorite, $Ca(ClO)_2+4H_2O$, are obtained, but owing to the ease with which they undergo decomposition these are not readily obtained pure.[1]

When sulphuric acid is added to a solution of bleaching powder, the whole of the chlorine is evolved in the free state; the hydrochloric acid and hypochlorous acid first formed acting on one another in the manner already described (vol. i., p. 319):

$$CaCl_2 + Ca(ClO)_2 + 2H_2SO_4 = 2CaSO_4 + 2HCl + 2HClO.$$
$$2HCl + 2HClO = 2Cl_2 + 2H_2O.$$

If hydrochloric acid be employed in place of sulphuric acid the reaction is as follows:—

$$CaCl_2 + Ca(OCl)_2 + 4HCl = 2CaCl_2 + 2H_2O + 2Cl_2.$$

Bleaching powder as well as the solution obtained by the action of chlorine on milk of lime is largely employed in the bleaching of cotton goods and of paper pulp.

The operations of bleaching cotton cloth are as follows:—

1. Boiling or "bucking" the cloth with milk of lime; 14 lbs. of cloth require about 1 lb. of lime, water being added to this in sufficient quantity to cover the cloth. In this process the resinous matters in the fibre are converted into lime-soaps.
2. Washing to remove lime and soluble salts.
3. Souring in dilute hydrochloric or sulphuric acid of specific gravity 1·0075 to decompose lime-soaps.
4. Washing to remove acid.
5. Bucking the cloth in dilute caustic soda-lye (170 lbs. of soda-ash and 80 lbs. of resin-soap to 3,500 lbs. of cloth) to remove fatty matters and dirt.
6. Washing and subsequent immersion in a clear dilute solution of bleaching powder of specific gravity 1·0025. This is called "chemicking."
7. Souring in very dilute hydrochloric or sulphuric acid of specific gravity 1·0075, then washing and drying.

The theory of bleaching has already been explained (see vol. i., pp. 164, 317).

The amount of available chlorine in bleaching powder is usually ascertained by adding to a solution of a known

[1] Kingzett, *Journ. Chem. Soc.* 1875, 404.

quantity a standard solution of sodium arsenite until the liquid no longer turns iodised starch paper blue, the arsenite being thus oxidised to arsenate, or by adding the bleaching powder solution to a solution of a known weight of ferrous sulphate in dilute sulphuric acid, until it is completely converted into ferric sulphate. Another method is to add to the bleaching powder a solution of potassium iodide, an amount of iodine equivalent to that of the available chlorine being liberated, which is determined by titration with sodium thiosulphate solution.

Calcium Chlorate, $Ca(ClO_3)_2$, is formed by leading chlorine into hot milk of lime, but cannot be obtained pure in this manner. The pure salt is obtained by neutralising calcium carbonate with chloric acid and crystallises with 2 mols. H_2O in rhombic prisms, which deliquesce in moist air and are very soluble in water.

Calcium and Sulphur.

211 *Calcium Monosulphide*, CaS, is obtained by heating the sulphate with powdered coal or by leading sulphuretted hydrogen or a mixture of carbon dioxide and the vapour of carbon bisulphide over incandescent lime (Schöne). It forms a yellowish-white mass insoluble in water, which in moist air smells of sulphuretted hydrogen. Calcium monosulphide is luminous in the dark after it has been exposed to light. This fact was noticed in the year 1750 by Marggraf, who obtained the sulphide by calcining gypsum with combustible matter. In 1768, Canton described a method of producing the same effect by igniting calcined oyster-shells with sulphur; hence this substance was long known under the name of Canton's phosphorus. Calcium sulphide is the chief constituent of alkali-makers' waste (p. 205).

Calcium Hydrosulphide, $Ca(SH)_2$, is best obtained by passing sulphuretted hydrogen into a cream of precipitated calcium hydroxide and rather less than four parts of water: it crystallises with 6 mols. H_2O in colourless prisms, which readily melt in their water of crystallisation.[1] It decomposes when warmed in a stream of sulphuretted hydrogen, yielding calcium sulphide, and is also decomposed by carbon dioxide with evolution of sulphuretted hydrogen and formation of calcium carbonate. It is sometimes used as a depilatory in tan works.

[1] Divers and Shmiddzu, *Journ. Chem. Soc.* 1884, i. 270.

Calcium Hydroxyhydrosulphide, $Ca(SH)OH$ is obtained by the action of a small quantity of water or of calcium hydroxide on the hydrosulphide,[1] and by the union of water and calcium sulphide, and forms crusts of small colourless four-sided needles; it readily dissolves in water, but the solution decomposes rapidly into calcium hydroxide and calcium hydrosulphide, the former separating out as a white precipitate. It combines with carbon bisulphide forming the *basic thiocarbonates*, $Ca(OH)_2$, $2CaCS_3 + 7H_2O$ and $2Ca(OH)$, $CaCS_3 + 10H_2O$, and it appears not unlikely that the presence of this substance causes the removal of carbon bisulphide from coal gas in the lime purifiers (vol. i., p. 779).

A number of other hydroxyhydrosulphides has been prepared, some of which crystallise well, but their constitution is at present doubtful. All of these hydrosulphides are oxidised by moist air with formation of calcium sulphite, thiosulphate, or sulphate, and usually with separation of free sulphur.

Calcium disulphide, CaS_2, is obtained in the form of yellow crystals containing 3 molecules of water when milk of lime is boiled with excess of sulphur and the filtered solution allowed to cool. *Calcium Pentasulphide*, CaS_5, is obtained by boiling calcium sulphide or hydroxide with excess of sulphur for a long time, and forms a reddish-yellow mass, which if treated with sulphuretted hydrogen in solution undergoes the reverse reaction, being converted into calcium hydrosulphide and sulphur.

Calcium Sulphite, $CaSO_3$, is obtained by mixing a solution of a calcium salt with that of a normal sulphite. It forms a white powder which dissolves in 800 parts of water. It is easily soluble in sulphurous acid, and if this solution be allowed to stand exposed to the air, six-sided needles separate out which have the composition $CaSO_3 + 2\ H_2O$. A solution of this salt in aqueous sulphurous acid which probably contains *calcium bisulphite*, $Ca(HSO_3)_2$, is met with in commerce, under the name of bisulphite of lime. It is obtained by passing sulphur dioxide into milk of lime, and is used by brewers to give beer stability.

212 *Calcium Sulphate*, $CaSO_4$, occurs in nature in the anhydrous state in the mineral anhydrite which is often found in limestone rocks, or together with deposits of common salt. More generally, however, the substance occurs as gypsum, $CaSO_4 + 2H_2O$, found frequently in large monosymmetric crystals and

[1] Divers and Shmiddzu, *Journ. Chem. Soc.* 1884, i. 270.

known as selenite. The crystalline form of selenite is shown in Figs. 97 to 99. The crystals are frequently twinned, and then exhibit the peculiar form shown in Fig. 100. It also occurs as fibrous gypsum or satin-spar, and as crystalline gypsum or alabaster.

This substance was known from early times as a mineral closely resembling calc-spar, because like the latter it became brittle on burning. In 1746 Pott described these two substances as being different earths, and stated that some chemists assumed that the substance artificially produced by the union of sulphuric acid with lime was gypsum, and termed it *gypsum artefactum*; in 1750 Marggraf showed that these two substances were identical.

Gypsum is sparingly soluble in water, 1 part of $CaSO_4 + 2H_2O$ dissolving according to Marignac[1]

at	0	18	24	32	38	41	53	72	86	99°
in	415	386	378	371	368	370	375	391	417	451

parts of water. The point of maximum solubility lies therefore between 32 and 41°. In presence of many other salts calcium

FIG. 97.

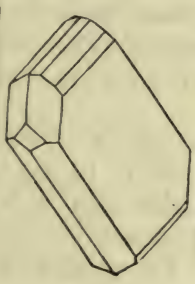


FIG. 98.

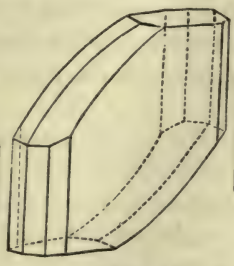


FIG. 99.

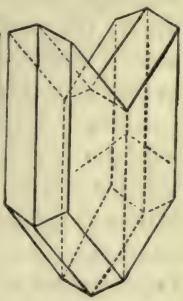


FIG. 100.

sulphate dissolves more readily, probably owing to the formation of more soluble double salts. Thus according to Anton 1 part of gypsum dissolves in 122 parts of a saturated solution of sodium chloride. Gypsum is tolerably soluble in boiling hydrochloric acid and nitric acid, and separates out from the acid solution on cooling in glittering silky needles. When heated with sulphuric acid to 100° it is changed into a porous mass, of which a part dissolves and separates out again on cooling. This

[1] *Ann. Chim. Phys.* 1874 (5), **1**, 274.

consists of microscopic prisms, which have the composition $CaSO_4 + H_2SO_4$: it is decomposed by water into its two constituents. Gypsum dissolves very readily in a solution of sodium thiosulphate.

When gypsum is heated at about 120—130° it loses water and is converted into burnt gypsum or plaster of Paris. This well-known substance when mixed with water combines with it, evolving heat, and subsequently solidifies, taking the form of the vessel in which it is contained. It is therefore largely used for ornamental plaster work, for making plaster casts, and as a cement. It was formerly supposed that the plaster consisted of anhydrous calcium sulphate, and that the setting was brought about by the direct combination of this with two molecules of water, reforming gypsum, but the researches of Le Chatelier[1] have shown that the properly burnt plaster still contains about 7–8 per cent. of water and consists of the hydrate $2CaSO_4 + H_2O$. When this is mixed with water part of this hydrate, which is much more soluble than either the anhydrous salt or the hydrate with two molecules of water, dissolves in the water to form a saturated solution; it very soon, however, becomes converted into the hydrate, $CaSO_4 + 2H_2O$, which being less soluble crystallises out, thus allowing the water to dissolve more of the hemihydrate; the same process is then repeated until the whole of the hemihydrate is converted into gypsum. The latter separates in long thin prisms which interlace to form the solid cake which remains.

If the gypsum be heated too strongly in the burning it only takes up water very slowly and is said to be dead-burnt; this is due to the whole of the water having been driven off leaving the anhydrous calcium sulphate. Such plaster when exposed to moist air gradually takes up 6–7 per cent. of water, and if then mixed with water it sets slowly, but with a normal hardness.

An artificial calcium sulphate is now prepared by precipitating a solution of calcium chloride with dilute sulphuric acid, and sold under the name of pearl hardening or annaline. It is used by paper-makers as a filling for writing paper. In addition to its employment for plaster work and casts, gypsum is also used as a manure.

Calcium Potassium Sulphate, $CaSO_4 + K_2SO_4 + H_2O$. This compound is formed when the solutions of the two salts are

[1] *Ann. des Mines*, 1887, 345.

mixed together (H. Rose). When an intimate mixture of equal weights of the anhydrous salts is stirred up with less than their weight of water, the mass becomes so suddenly solid that it cannot be poured out of the vessel. If four to five parts of water are employed, the solidification takes place somewhat more slowly but still more rapidly than in the case of gypsum alone. Casts made of this mixture possess a polished surface and are in this respect superior to those made of gypsum.

Calcium Sodium Sulphate, $CaSO_4 + Na_2SO_4$, occurs in nature as the mineral glauberite. Sodium sulphate does not act upon plaster of Paris as potassium sulphate does. If, however, a mixture of one part of precipitated calcium sulphate and fifty parts of Glauber's salt be heated to 80° with twenty-five parts of water, a mass of needle-shaped crystals is obtained, which have the formula $CaSO_4 + 2Na_2SO_4 + 2H_2O$, and these when further heated are transformed into small crystals of glauberite (Fritzsche).

Calcium Thiosulphate, $CaS_2O_3 + 6H_2O$, is prepared by heating calcium sulphite with sulphur and water. It forms six-sided asymmetric prisms, soluble in their own weight of cold water. When the solution is heated to 60° the salt is decomposed with evolution of sulphur. This salt is used in the production of antimony cinnabar, Sb_2OS_2.

Calcium and the Elements of the Nitrogen Group.

213 *Calcium Nitrate*, $Ca(NO_3)_2$.—The alchemist Baldewein or Balduinus first prepared this compound whilst searching for a method of absorbing the "Spiritus mundi." He dissolved chalk in nitric acid, and observing that the solid product became rapidly moist on exposure to air, concluded that this substance would prove to be of great power. In the year 1674 he noticed that the solid residue after being heated and then exposed to sunshine appeared luminous in the dark, and from this time the compound prepared as above was termed Baldwin's phosphorus: Calcium nitrate forms monosymmetric crystals containing four molecules of water, is very deliquescent, and dissolves readily in alcohol as well as in water. The anhydrous salt is a white porous mass, and is often found as an efflorescence on the walls of stables and other places through which urine and other

organic liquids percolate. The name lime-saltpetre, or wall-saltpetre, has been given to this salt, which was formerly universally employed for the artificial preparation of nitre.

Calcium Phosphide.—This substance is best prepared by heating lime to a moderate red-heat in a Hessian crucible, through the lid of which passes a piece of gas pipe reaching to the bottom, and sufficiently wide to allow of the passage of sticks of phosphorus which are added in pieces weighing about 15 grams. It forms a very hard dark mass the surface of which is frequently iridescent, the product also containing calcium pyrophosphate.[1] It is decomposed by water with formation of liquid hydrogen phosphide, P_2H_4, and is employed for the preparation of this substance (vol. i., p. 571).

Phosphates of Calcium. Normal Calcium Orthophosphate or *Bone-phosphate*, $Ca_3(PO_4)_2$.—This compound occurs together with calcium fluoride in apatite, $3Ca_3(PO_4)_2 + CaF_2$ or $Ca_3(PO_4)_2 + Ca_2(PO_4)F$; in which a portion of the fluorine is sometimes replaced by chlorine. Phosphorite and estramadurite are massive varieties of apatite which occur in Estramadura, in Spain. Coprolites, which are found in many sedimentary deposits, and doubtless have an animal origin, consist mainly of calcium orthophosphate. Another pure form of the same compound is the mineral osteolite, and it also occurs as sombrerite, a mineral found on some of the small islands of the Antilles, especially Sombrero, and containing crystals of the mineral ornithite $Ca_3(PO_4)_2 + 2H_2O$. Calcium phosphate is also the chief inorganic constituent of bones, forming about 80 per cent. of burnt bones; the other constituents being magnesium phosphate, calcium carbonate, and calcium fluoride.

Pure calcium phosphate is obtained as a white precipitate by adding an excess of common sodium phosphate to an ammoniacal solution of chloride of calcium. It is nearly insoluble in water but is decomposed on long boiling into an insoluble basic salt, $Ca_3(PO_4)_2 + Ca_2(PO_4)OH$, and a soluble acid salt which dissolves. This decomposition takes place slowly in the cold, and for this reason an exact determination of the solubility of the orthophosphate is impossible.[2] Calcium orthophosphate dissolves readily in water containing ammoniacal salts, sodium nitrate, common salt, and other salts. It is also readily soluble

[1] Gattermann and Haussknecht, *Ber.* 1890, **23**, 1176.

[2] R. Warington, *Journ. Chem. Soc.* 1873, 983.

in all acids, even in aqueous carbonic acid. This explains the absorption of calcium phosphate by the roots of plants, which accumulate it in the seeds and fruit.

Mono-hydrogen Calcium Orthophosphate, $HCaPO_4$.—When a solution of calcium chloride is mixed with one of ordinary sodium phosphate, a white crystalline precipitate of the above compound containing two molecules of water of crystallisation is thrown down. This compound occurs in urinary concretions, and is sometimes deposited from urine in microscopic crystals grouped in rosettes or stellæ, and known as stellar phosphate.

Tetra-hydrogen Calcium Phosphate, $H_4Ca(PO_4)_2$.—This salt is obtained in rhombic tables by dissolving either of the foregoing salts in the requisite quantity of phosphoric acid and allowing the solution to evaporate spontaneously. If this be treated with cold water the hydrated mono-hydrogen phosphate $HCaPO_4 + 2H_2O$ is formed, whilst with boiling water the same salt is produced in the anhydrous form (Erlenmeyer).

Superphosphate of Lime.—A mixture of the last-mentioned compound and calcium sulphate is manufactured on the large scale, and known in commerce as *superphosphate of lime.* It is usually prepared by acting on bone-ash, coprolites, phosphorites, or other form of mineral phosphate by two-thirds of its weight of sulphuric acid. This mixture is largely employed as a manure, especially for root crops. About 4,000,000 tons of superphosphates were manufactured in Great Britain in 1895, the average value being about £2 10*s.* per ton.

Calcium Hypophosphite, $Ca(PO_2H_2)_2$, is used in medicine and is prepared by boiling phosphorus with milk of lime. On evaporating the clear solution, the salt crystallises in bright, six-sided monosymmetric prisms.

Calcium and Carbon.

214 *Calcium Carbide*, CaC_2.—This compound was obtained by Moissan by heating pure lime and sugar charcoal to a very high temperature in an electrical furnace, the following reaction taking place:

$$CaO + 3C = CaC_2 + CO.$$

It forms golden-yellow lustrous opaque crystals which are

decomposed by water with formation of the hydrocarbon acetylene :[1]

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

A crude carbide is now prepared on the large scale by heating a mixture of limestone with coke or small coal in an electrical furnace, the product having a greyish-black appearance. It is employed for the preparation of acetylene for lighting purposes, the illuminating power of this gas being 12-15 times greater than that of ordinary coal-gas.

Calcium Carbonate, $CaCO_3$.—This compound occurs widely distributed and in enormous masses in nature forming whole mountain ranges, being found as limestone of various kinds, marble, calc-spar, and chalk. It also forms the greater part of egg-shells, shells of mollusca and coral, and is contained together with calcium phosphate in burnt bones. Calcium carbonate is dimorphous : it exists in the first place as *calc-spar*, which has a specific gravity varying from 2·70 to 2·75, and crystallises in hexagonal and chiefly hemihedral forms. Some of the more important of these are seen in Figs. 101 to 109, a common twin-crystal being shown in Fig. 109. The primary form, Fig. 101, is a rhombohedron having angles of 104°5′ and 74°5′. The second form of calcium carbonate is known as *arragonite*, having a specific gravity of from 2·92 to 3·28, and crystallising in the form of rhombic prisms, Figs. 110, 111. Another crystalline form often exhibited by arragonite is that of the penetration twins, shown in Fig. 112. A distinction between the two minerals was first drawn by Werner in 1788, and Haüy showed somewhat later that they crystallised in two distinctly different forms. For many years this difference was believed to be due to the presence of strontia in arragonite, and it was not until 1819, when Mitscherlich discovered the law of dimorphism, that it was satisfactorily understood.

When a calcium salt is precipitated by the carbonate of an alkali metal, or when carbon dioxide is passed through lime-water, the precipitate which falls down is at first flocculent and amorphous. That formed by passing a small quantity of carbon dioxide through cold lime-water soon becomes crystalline, the crystals being those of calc-spar, whilst arragonitic crystals are deposited when the lime-water is hot (G. Rose). Calc-spar crystals are deposited when a solution of calcium carbonate in

[1] *Compt. Rend.* 1894, **118**, 50.

carbonic acid is allowed to evaporate spontaneously at the common temperature; but if the solution be heated to 90° arragonite crystals separate out.

One liter of water dissolves 14 milligrams of calcium carbonate at 18°. In presence of free ammonia or ammonium carbonate it is still less soluble. On the other hand, it readily dissolves in water containing carbonic acid in solution, this phenomenon having been first investigated by Cavendish in 1767. One liter of water

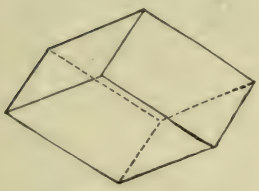


Fig. 101.

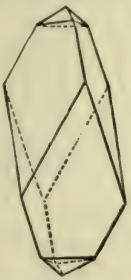


Fig. 102.

Fig. 103.

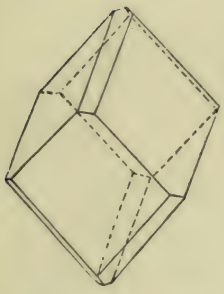


Fig. 104.

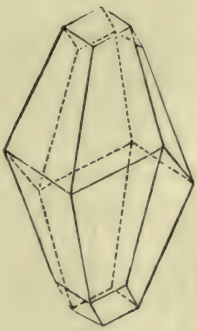


Fig. 105.

Fig. 106.

Fig. 107.

saturated with carbon dioxide dissolves at 0° 0·70 gram of calcium carbonate, and at 10°, 0.88 gram. The solubility increases under an increase of pressure up to 3 grams per liter, but not beyond this point (Caro). If such a solution be allowed to stand at the ordinary temperature, six-sided prisms, having the composition $CaCO_3 + 5H_2O$, separate out. These crystals, which lose their water at 19°, are sometimes found in the pipes of pumps and also adhering to confervæ in ponds. When a solution of calcium carbonate in carbonic acid water is boiled, the liquid still con-

tains in solution 34 milligrams of calcium carbonate per liter, and this solution does not render lime-water turbid.[1]

When calcium carbonate is heated to about 550° it commences to decompose into quicklime and carbon dioxide, but if the latter

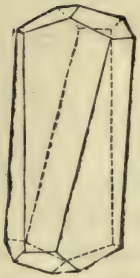


FIG. 108.

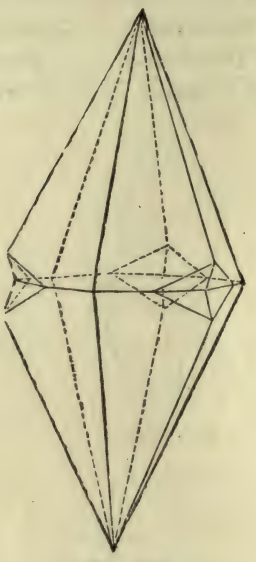


FIG. 109.

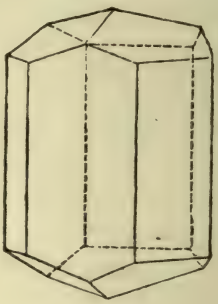


FIG. 110.

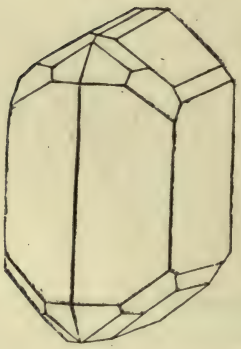


FIG. 111.

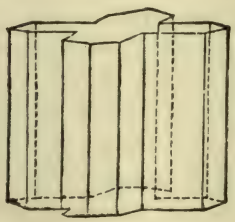


FIG. 112.

is not removed the decomposition is not complete, even if the temperature be raised considerably (*cf.* p. 110). When very strongly heated in closed vessels, it melts and solidifies on cooling to a marble-like mass.

[1] Hofmann, *Jahresb.* 1865.

Calcium and Silicon.

215 *Calcium Silicates.*—These compounds exist in almost all mineral silicates, certain of these consisting mainly if not altogether of silicates of calcium and isomorphous metals. Among the more important of these are wollastonite, $CaSiO_3$; okenite, $CaH_2Si_2O_6 + H_2O$; xonalite, $4CaSiO_3 + H_2O$; apophyllite, $4H_2CaSi_2O_6 + KF + 4H_2O$. Le Chatelier [1] has also prepared the following anhydrous silicates artificially: $CaSiO_3$, Ca_2SiO_4, $Ca_3Si_2O_7$, and Ca_3SiO_5.

Mortars and Cements.

216 Ordinary mortar is a mixture of one part of lime made into a paste with water and mixed with three to four parts of sharp sand, the completeness of the subsequent hardening being dependent on the proper admixture of the ingredients. Mortar sets sufficiently to give stability to a structure in a few days, this being brought about almost entirely by the loss of water. It thus becomes porous and the lime is then gradually attacked by the carbon dioxide of the air which converts it slowly but completely into calcium carbonate, the mortar gradually hardening and cementing the sand and building material together. Many years or even centuries elapse before the maximum of hardness is reached, and it appears that at the same time an extremely slow combination of the silica and lime takes place; thus Petzholdt [2] found 2·1 per cent. of combined silica in a mortar 100 years old, and 6·2 per cent. in a sample 300 years old, the lime originally used only containing at most 0·11 per cent. Under ordinary circumstances, however, this action plays no part in the hardening process.

Hydraulic Mortars.—When limestone contains from about 8 per cent. upwards of clay, the lime obtained from it yields a mortar which has the property of setting under water and is therefore known as *hydraulic mortar.* Such mortars may also be obtained from "fat" lime by mixing it with certain silicates; thus many Roman works are still standing which were built with a hydraulic mortar prepared from lime and a volcanic tufa

[1] *Annales des Mines*, 1887, 345.
[2] *J. Pr. Chem.* 1839, **16**, 91; **17**, 464.

termed *puzzuolana*, found at Puzzuoli near Mount Vesuvius, and consisting of a mixture of various silicates. This mortar is described both by Pliny and Vitruvius. In place of puzzuolana baked clay and numerous other silicates may be employed.

Cements.—These substances, which differ from hydraulic mortars inasmuch as they do not contain any admixture of free lime, are obtained either by the careful heating of argillaceous limestone, or by calcining a mixture of a suitable clay with the requisite quantity of limestone. *Roman cement*, originally manufactured by James Parker in 1796, was prepared in the former manner, the crude material employed being originally the clay nodules found on the coast of Essex and Kent, termed *septaria*. *Portland cement* is manufactured from limestone and clay, most of the manufacture in this country being carried out in the valley of the Medway, the river mud of which is very suitable for the purpose. The limestone and clay are ground together, and the mixture, termed "slip" or "slurry," after drying is carefully burnt in a kiln; the fuel employed is coke, alternate layers of the mixture and fuel being placed in the kiln. The carbon dioxide is thus completely eliminated and the lime formed combines with the clay forming chiefly calcium silicate and aluminate. The cement clinker drawn from the kiln is broken up and then ground between millstones. The following analyses of English (1 and 2) and German (3 and 4) Portland cements give the composition of the substance:—

	1.	2.	3.	4.
Lime	59·06	55·06	62·81	57·83
Silica	24·07	22·92	23·22	23·81
Alumina . . .	6·92	8·00	5·27	9·38
Ferric oxide . .	3·41	5·46	2·00	5·22
Magnesia . . .	0·82	0·77	1·14	1·35
Potash	0·73	1·13	1·27	0·59
Soda	0·87	1·70		0·71
Calcium sulphate	2·85	1·75	1·30	1·11
Clay	1·47	2·27	2·54	—
Sand				

The Setting of Cements.—The cause of the setting of cements has been the subject of much discussion during the past century; until recently the explanations given were very incomplete, but the researches of Le Chatelier[1] have now thrown

[1] *Annales des Mines*, 1887, 345.

considerable light on the subject. He has examined the action of polarised light on the crystalline substances which can be observed under the microscope in a thin section of Portland cement, and compared these optical properties with those of a number of calcium silicates and aluminates which he prepared artificially. From these experiments he concludes that the chief constituents of cement are tricalcium orthosilicate, $3CaO,SiO_2$; tricalcium aluminate, $3CaO,Al_2O_3$,; and tricalcium aluminoferrite, $3CaO, 2(AlFe)_2O_3$, properly made cement containing no free lime. On the addition of water, the calcium compounds are decomposed with formation at first of free calcium hydroxide, and there are then formed crystalline hydrated calcium silicate and aluminate, the crystals of which form an interlaced mass thus bringing about the setting of the cement. The setting takes place long before the formation of the hydrated crystals is complete, and as the action goes on the cement becomes continuously harder. There is therefore no such difference between the setting and hardening actions as in the case of ordinary mortar.

Detection and Estimation of Calcium.

217 The fact that certain compounds of calcium impart a red colour to the flame of the spirit-lamp was first observed by Ribbentrop in 1796. The spectrum of a non-luminous gas flame tinted by calcium chloride exhibits a number of lines of which the green line Caβ is the most characteristic, the orange line Caα being also very prominent (see Fig. 14 p. 136). This spectrum is mainly due to the chloride and oxide and not to the vapour of the metal itself, and is also yielded by calcium compounds which do not volatilise in the flame, when they are moistened with hydrochloric acid and placed on a platinum wire in the hottest portion of the flame. Certain silicates containing calcium which are not decomposed by hydrochloric acid must be first heated with ammonium fluoride, the residue then decomposed by sulphuric acid, and treated as above. By means of the spectroscope as small a quantity as 0·00006 of a mgrm. of calcium chloride or similar salt may be detected. At the temperature of the electric arc the calcium compounds show the spectrum of metallic calcium, consisting of a number of fine bright lines.

Calcium may be separated from the alkali-metals by the

addition of a solution of ammonium carbonate, calcium carbonate being precipitated. As has been stated, this latter salt is not altogether insoluble in water, and it is, therefore, preferable to precipitate the lime as calcium oxalate by the addition of ammonium oxalate in neutral or ammoniacal solution, this salt being almost completely insoluble in water. This reaction is usually employed for the estimation of calcium; the washed and dried precipitate, which has the composition $CaC_2O_4 + 2H_2O$ is either gently ignited, by which means it is converted into the carbonate; or it is strongly ignited, when the carbonate is converted into caustic lime. Calcium is also occasionally estimated as the sulphate. The precipitation by sulphuric acid must, however, be made in presence of alcohol, and the precipitate must also be washed with the same liquid.

The atomic weight of calcium was first accurately determined by Erdmann and Marchand,[1] by the the ignition of calc-spar and of precipitated calcium carbonate. From their experiments it appears that when O = 15·88 and C = 11·91 the atomic weight of calcium is 39·68, 39·70, 39·73, or as a mean of the three numbers 39·7 (pp. 10, 11). Baup[2] obtained the number 39·67 as the result of the analysis of organic lime salts.

STRONTIUM, Sr = 87·0.

218 The name of this element is derived from that of Strontian, a village in Argyllshire, in which a peculiar mineral, strontium carbonate or strontianite, was first found. At first this mineral was mistaken for barium carbonate, but in the year 1790 Crawford suggested that it contained a peculiar earth, founding his opinion upon experiments which had been made on the mineral by Cruikshank. This was confirmed in 1792 by Hope,[3] and independently by Klaproth,[4] a year afterwards. Sir Humphry Davy in 1807 first obtained the metal strontium.

Strontium occurs chiefly as the sulphate or *celestine* $SrSO_4$, and as the carbonate or *strontianite* $SrCO_3$. Many specimens of arragonite and of calc-spar contain small quantities of stron-

[1] *Annalen*, 1844, **52**, 210; 1848, **66**, 219. [2] *Annalen*, 1844, **52**, 212.
[3] Account of a mineral from Strontian, *Trans. Roy. Soc. Edinb.* **4**, 3.
[4] *Crell. Ann.* 1793, **2**, 189 and 1794, **1**, 99.

tium carbonate; and the same may be said of many kinds of limestone, marble and chalk, although the strontium is generally present only in very small traces. *Baryto-celestine* is a mineral which contains the sulphates of barium and strontium. and the latter compound occurs also in small quantities in different varieties of heavy spar. Strontium occurs as a silicate in *brewsterite*, $H_4(BaSr)Al_2Si_6O_{18} + 3H_2O$. Small quantities of the chloride and sulphate of strontium occur in solution in many brine-springs as well as in different mineral waters. It is also present in chalk waters, such as that of the London basin. Strontium has also been found in sea-water and in the ashes of *Fucus vesiculosus*.

Preparation of Metallic Strontium.—Davy obtained the metal strontium by the electrolysis of either the moistened hydroxide or of chloride of strontium. It can be more readily prepared according to the method employed by Bunsen and Matthiessen.[1] A small porcelain crucible having a porous cell in the middle is filled with anhydrous chloride of strontium, mixed with a little sal-ammoniac, the level of the salt within the cell being considerably higher than in the crucible. The negative pole which is placed within the porous cell consists of a very thin iron wire, wound round a thicker one, and then covered with a piece of tobacco-pipe stem so that only $\frac{1}{16}$th of an inch of it appears below; the positive pole is an iron cylinder placed in the crucible round the porous cell. The heat is regulated during the experiment so that a crust may form in the cell. The metal then collects under this crust without coming in contact with the oxygen of the air. By this method pieces of the metal weighing half a gram are sometimes obtained.

Metallic strontium can also be obtained, according to B. Franz,[2] by repeatedly heating a saturated solution of chloride of strontium with an amalgam of 250 grams of sodium and one kilogram of mercury to a temperature of 90°. The strontium amalgam thus obtained is quickly washed with water, and dried between folds of filter paper. It is then heated in a current of hydrogen in an iron crucible, by which means all the mercury is volatilised and a regulus of strontium remains behind.

Strontium is a pale yellow metal somewhat harder than calcium and lead. It may be hammered out into thin plates, and possesses a specific gravity of 2·5. It melts at a moderate

[1] *Journ. Chem. Soc.* 1856, 107. [2] *J. Pr. Chem.* 1869, **107**, 253.

red-heat, and is more electro-negative than calcium and the alkali-metals. It oxidises quickly on exposure to the air, burns brilliantly when heated, and decomposes water violently.

STRONTIUM COMPOUNDS.

Strontium and Oxygen.

219 *Strontium Monoxide or Caustic Strontia*, SrO.—This substance is obtained by the ignition of the nitrate in the form of a greyish-white porous mass, which becomes crystalline at about 2,500° and melts at about 3,000° (Moissan). When brought into contact with a small quantity of water the monoxide unites with it to form a white powder of *strontium hydroxide*, $Sr(OH)_2$. This body possesses a specific gravity of 3·625, and when strongly heated is reconverted into strontia. The hydroxide is easily soluble in hot water, and the solution, on cooling, deposits transparent quadratic crystals of the hydrate $Sr(OH)_2 + 8H_2O$: 100 parts of cold water dissolve 2·0 and of boiling water 41·66 parts of the crystals. Strontia water has a strongly alkaline reaction and possesses caustic properties less marked than the solutions of the alkalis.

Strontium Dioxide, SrO_2.—Pearly scales of the hydrated dioxide, $SrO_2 + 8H_2O$, separate out on mixing a solution of the hydroxide with hydrogen dioxide; these lose water on heating, leaving the anhydrous dioxide as a light white powder which does not melt at a red-heat but gradually loses oxygen (Schöne).

Salts of Strontium.

220 *Strontium Chloride*, $SrCl_2$, is obtained by dissolving strontianite in hydrochloric acid. The hot concentrated solution deposits on cooling, long hexagonal needles, $SrCl_2 + 6H_2O$, which are isomorphous with the corresponding hydrate of calcium chloride. They possess a sharp bitter taste, have a specific gravity of 1·603, and effloresce on exposure to the air. On heating, these crystals yield the anhydrous salt as a white powder, which melts at a high temperature to a white semi-

transparent glassy mass having a specific gravity of 2·96. According to Mulder 100 parts of water dissolve :—

At	0°	20°	40°	60°	80°	100°	118°·8
$SrCl_2$	44·2	53·9	66·7	83·1	92·4	101·9	116·4.

Chloride of strontium also dissolves in alcohol. The commercial salt frequently contains calcium chloride, from which it may be purified by repeated crystallisation from hot water.

Strontium Sulphate, $SrSO_4$, is found in large well-developed rhombic crystals and as a fibrous amorphous mass. It frequently possesses a light blue colour, whence it takes its name celestine (*cœlestis*). When sulphuric acid or a soluble sulphate is added to a solution of a strontium salt, the sulphate is thrown down as a white precipitate possessing a specific gravity of 3·707 and fusing when strongly heated. It is but very slightly soluble in cold, and still less soluble in boiling water. One liter of water at 18° dissolves 0·107 gram. (Kohlrausch and Rose). Strontium sulphate is much more easily soluble in acids and in solution of common salt, as well as in other salt solutions, but less soluble in sulphates or dilute sulphuric acid, and is completely decomposed by boiling with a solution of an alkali carbonate. When the salt is dissolved in hot concentrated sulphuric acid, crystals of celestine separate out on cooling, and when it is treated with concentrated sulphuric acid at 100°, and the solution digested with an excess of the salt at a somewhat higher temperature, the compound $H_2SO_4 + SrSO_4$ separates out as a granular crystalline powder, which when exposed to moist air changes into small glittering tablets having the composition $H_2SO_4 + SrSO_4 + H_2O$.

Strontium Nitrate, $Sr(NO_3)_2$, is obtained by dissolving the carbonate in warm dilute nitric acid. When the solution is evaporated down, the anhydrous salt separates out in transparent octohedra or in combinations of the octohedron and the cube. Strontium nitrate possesses a cooling taste. It has a specific gravity of 2·962 (Schröder), and when thrown on to red-hot charcoal it deflagrates, burning with a red flame. When a dilute solution is cooled down, the hydrate, $Sr(NO_3)_2 + 4H_2O$, separates out in large well-developed monosymmetric crystals which quickly effloresce on exposure to the air. One hundred parts of water dissolve, according to Mulder:

At	10°	20°	40°	60°	80°	100°	107°·9
$Sr(NO_3)_2$	40·16	70·8	91·3	94·6	97·2	101·1	102·9

Strontium nitrate is insoluble in concentrated nitric acid and only very slightly soluble in absolute alcohol. It is largely used for pyrotechnic purposes.

Strontium Carbonate, $SrCO_3$, occurs as strontianite in crystals which are isomorphous with those of arragonite. This compound is obtained in the form of a white impalpable powder having a specific gravity of 3·62, if a strontium salt be precipitated by an alkaline carbonate. When gently ignited it loses all its carbon dioxide and is converted into strontia. According to Kohlrausch and Rose 1 liter of water dissolves 11·0 mgrms. of this salt at 18°. It is less soluble in water containing ammonia, but dissolves considerably in a solution of sal-ammoniac and of ammonium nitrate. When boiled with sal-ammoniac it is converted into strontium chloride.

Detection and Estimation of Strontium.

221 Strontium salts colour the flame a magnificent crimson. When examined by the spectroscope the spectrum is found to consist of numerous bright lines due to the salts and oxide of the metal, of which eight are specially characteristic, six in the red, one in the orange, and one in the blue. The orange line, termed Sr a, the red, Sr β, and Sr γ, and the blue line, Sr δ, are the most intense, and therefore the most valuable for the discrimination of this element. By means of spectrum analysis $\frac{6}{100000}$ mgrm. of strontium chloride can be detected. H. Fox Talbot[1] was the first to describe the spectrum of strontium. He examined the spectrum of the red fire of theatres and distinguished many of the strontium lines especially the blue line, Sr δ (p. 123). In order to detect strontium the bead either alone or moistened with hydrochloric acid is brought into the flame. If strontium be supposed to be present as sulphate the bead is held for a few moments in the reducing portion of the flame and then moistened with hydrochloric acid in order to convert the strontium sulphide which is formed into strontium chloride. The strontium salts containing non-volatile acids are melted on a platinum wire with a small quantity of sodium carbonate. The fused bead is then reduced to a fine powder and dissolved in a little hot water, and the residue, which contains strontium carbonate, moistened with

[1] *Brewster's Journ. of Science*, 1826, **5**.

hydrochloric acid, and the chloride brought on a wire into the non-luminous flame.

Strontium is separated from the alkali-metals by precipitation with ammonium carbonate. Strontium is usually determined quantitatively as the sulphate by precipitating the solution with sulphuric acid in the presence of alcohol and washing the precipitate with a weaker alcohol. In order to separate it from calcium the substances are converted into nitrates and these treated with absolute alcohol or amyl alcohol[1] which leave the nitrate of strontium undissolved.

Atomic Weight of Strontium.—The atomic weight of strontium was determined by Marignac[2] from the amount of silver required to precipitate a known weight of pure crystallised strontium chloride, and also from the amount of strontium sulphate formed from the chloride; he thus obtained the numbers Sr = 86·64 and 86·76 respectively (O = 15·88). Richards[3] from the determination of the amount of silver required to precipitate a known quantity of pure strontium bromide and the quantity of silver bromide formed, obtained as the average of a number of closely agreeing experiments the number 87·0 (O = 15·88).

BARIUM, Ba = 136·41.

222 Our knowledge of the barium compounds commences with that of the natural sulphate or heavy-spar. This substance was first examined in the year 1602, by a Bolognese shoemaker, V. Casciorolus, who noticed that it possessed the remarkable property of becoming phosphorescent when ignited with combustible matter. To this material the discoverer gave the name of *lapis solis*, but it became better known as Bolognian or Bononian phosphorus, from the place in which it was first prepared, whence specimens of the shoemaker's handiwork found their way into the laboratories of the alchemists of the time. The mineral which yielded this phosphorus, termed Bolognian spar, was first believed to be a peculiar kind of gypsum, and hence it was termed *gypsum spathosum*. In

[1] Browning, *Amer. J. Sci.* 1892, **43**, 50.
[2] *Annalen*, 1858, **106**, 165.
[3] *Zeit. Anorg. Chem.* 1895, **8**, 253.

consequence of its high specific gravity, Cronstedt termed it *marmor metallicum*, and Marggraf in 1750, finding that it contained sulphuric acid, ranked it amongst what were then termed the heavy fluor-spars. The nature of this mineral remained for some time obscure, and the learned mineralogist v. Justi wrote in 1760 concerning it as follows: "Our analysis has here reached its limits; we know of no smelting operation by which anything can be got out of this spar. Many profound chemists and skilful assayers have here tried their art in vain." The next step in our knowledge of this subject was made in the year 1774, when Scheele, who was engaged in his investigation on the black oxide of manganese, examined a specimen of this mineral which he found to contain a new earth, and this when brought in contact with sulphuric acid yielded a salt insoluble in water, which could be brought into a soluble condition by ignition with carbon and an alkali. Gahn afterwards showed that this earth was contained in heavy-spar, and Bergman gave it the name *terra ponderosa*. Guyton de Morveau in 1779 proposed the name barote (from βαρύς, heavy), and this name, slightly altered to baryta by Lavoisier, was soon generally adopted. The suggestion that this earth was the oxide of a metal was frequently made, but the fact was not proved until after Davy's discovery of the decomposition of the alkalis.

Barium occurs in nature chiefly as the sulphate or heavy-spar, $BaSO_4$, which is often found together with galena and other metallic ores, though also found not associated with metallic veins. Another source of barium compounds, less widely distributed, is the carbonate or witherite, $BaCO_3$, whilst other minerals containing barium are barytocelestine, $(BaSrCa)SO_4$, barytocalcite, $BaCO_3+CaCO_3$, alstonite, $(BaCa)SO_4$, and psilomelane $(MnBa)O + MnO_2$. Many other ores of manganese, especially manganese dioxide, contain small quantities of barium. Barium also occurs as an essential constituent of certain silicates; thus, for instance, brewsterite, $H_4(SrBa)Al_2Si_6O_{18}+3H_2O$, harmotome, $H_2(K_2Ba)Al_2Si_5O_{15} + 4H_2O$ and hyalophane or baryta-felspar, $(K_2Ba)2Al_2Si_3O_{24}$. Many other felspathic rocks also contain traces of barium, and this element occurs likewise in several other minerals. Traces are found in mineral waters and in sea-water. Thus, for instance, the old sulphur well at Harrogate contains 6·6 grains of barium chloride per gallon (Hayton Davis).[1] From sea-water, barium finds its way into sea-plants,

[1] Thorpe, *Phil. Mag.* 1876 [5], **2**, 52.

and in smaller quantities into the shells and skeletons of sea-animals.

Preparation of Metallic Barium.—Davy's first attempts to obtain metallic barium were not very successful. He endeavoured first to obtain it by the electrolysis of baryta. Afterwards finding that this did not succeed he prepared it from an amalgam, having heard from Berzelius that he and Pontin had succeeded in obtaining it in that way. Davy repeated these experiments and electrolysed baryta, barium chloride, and other barium salts in presence of mercury, heating the amalgam which was thus formed in a tube containing rock oil, when the barium was left behind as a silver-white powder. According to Bunsen's process,[1] the metal may be obtained by electrolysing a thick mixture of very dilute hydrochloric acid and barium chloride at a temperature of 100° in presence of mercury. In this way a crystalline barium amalgam may be obtained, which, on heating, leaves metallic barium behind in the form of a tarnished porous mass, the cavities of which sometimes exhibit a silver-white surface. The experiment is however more successful when a galvanic current is passed through barium chloride in a state of fusion, the negative pole consisting of a fine harpsichord wire on which the barium is deposited in the form of small globules. It oxidises very quickly, and burns brilliantly when heated in the air.[2]

The melting-point of barium appears to be higher than that of cast-iron (Frey).

COMPOUNDS OF BARIUM.

Barium and Oxygen.

223 *Barium Monoxide or Baryta*, BaO, is formed when the metal burns in the air, but is usually obtained by heating the nitrate in an iron crucible, until no further evolution of red fumes is observed. The mass fuses and is apt to froth over unless care be taken. Mohr has proposed to mix the nitrate with its own weight of sulphate of barium; this prevents the frothing, and for many purposes the presence of insoluble barium sulphate does not matter. If only a small quantity of baryta is

[1] *Pogg. Ann.* 1854, **91**, 619. [2] Matthiessen, *Annalen*, 1855, **93**, 277.

required it is best obtained by igniting the iodate, which gives off its iodine and five-sixths of its oxygen without fusing or frothing :—

$$2Ba(IO_3)_2 = 2BaO + 2I_2 + 5O_2.$$

It is also prepared by heating barium carbonate to a white-heat, the reaction proceeding more readily if this be mixed with one-tenth of its weight of lamp-black or charcoal, carbon monoxide being then evolved :—

$$BaCO_3 + 2C = BaO + 3CO.$$

Baryta is thus obtained as a greyish-white porous mass, which has a specific gravity of 4·73 (Karsten), 5·46 (Filhol), and melts at about 2,000°, crystallising out on cooling in cubes, which have a specific gravity of 5·72. It combines with water with great evolution of heat forming the hydroxide, becoming incandescent if only sprinkled with water. It also unites with oxygen at a red-heat, the oxygen being evolved on further heating, and it is therefore now used for the manufacture of oxygen (vol. i., p. 221).

Barium Hydroxide, $Ba(OH)_2$, is formed as a white powder by the reaction just described. The hydroxide melts at a low red-heat, forming an oily liquid, which on cooling solidifies to a crystalline mass, and this does not give off water even when more strongly heated. It is prepared on the large scale from barium sulphide, which is heated in earthenware retorts, into which a current of moist carbonic acid is passed. Superheated steam is then passed over the carbonate, when the following decomposition takes place :

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2.$$

It has a specific gravity of 4·495 (Filhol), and when brought in contact with water forms a crystalline hydrate, $Ba(OH)_2 + 8H_2O$. This hydrate is soluble, and when a saturated solution is cooled it separates out in quadratic prisms which are isomorphous with strontium hydrate. On exposure to air these crystals fall to a white powder with loss of seven molecules of water. One hundred parts of water dissolve :

At	0°	20°	40°	60°	80°
$Ba(OH)_2$	1·65	3·9	8·3	21·0	101·5 parts.

A solution of the hydroxide is termed *baryta-water*, and is largely used in the processes of chemical analysis. It has a more strongly alkaline reaction than lime-water, and rapidly absorbs carbon dioxide. It is employed, as has been stated in vol. i., p. 540, for the determination of the carbonic acid contained in the atmosphere, for which purpose it must be free from alkali.

Caustic baryta is now employed in the processes of sugar-refining, instead of lime, as baryta forms an insoluble compound, $C_{12}H_{22}O_{11}BaO$, with cane sugar, whilst lime forms a soluble compound with sugar but precipitates the acids and nitrogenous substances from the juice. The barium-sugar compound is easily decomposed by suspending it in water and subjecting it to the action of carbonic acid gas, when the sugar dissolves, and insoluble barium carbonate is precipitated.

Barium Dioxide, BaO_2.—When heated to redness in a current of dry oxygen, pure baryta absorbs the gas with rapidity, forming the dioxide (Gay-Lussac and Thénard); it is also formed by heating baryta and potassium chlorate to low redness (Liebig and Wöhler). The hydroxide when heated to redness in a current of air also yields the dioxide (Boussingault). In Brin's process for the manufacture of oxygen it is obtained as an intermediate product by heating pieces of baryta of the size of walnuts to 700° in steel retorts, and passing air through these under an additional pressure of 15 lbs. per square inch. The product obtained by any of these methods is a greyish porous mass and usually contains silica, lime, and also ferric oxide obtained from the vessels in which it is prepared. To obtain it in the pure state it is treated in the manner already described under hydrogen peroxide (vol. i., p. 309), and then when dried at 130° forms an impalpable white powder, which can hardly be distinguished from magnesia. It fuses at a bright red-heat with loss of one atom of oxygen, and combines with water to form the hydrate $BaO_2 + 8H_2O$, which crystallises in microscopic hexagonal plates, which are only very slightly soluble in water.

Barium and the Halogens.

224 *Barium Chloride*, $BaCl_2$, is most readily obtained by dissolving witherite in dilute hydrochloric acid. As, however, this mineral contains calcium, lead, iron, and manganese com-

pounds, an excess of barium carbonate is added to the solution and the liquid allowed to remain in contact with it for some time. In this way the oxides of the above metals are precipitated and the rapidity of the precipitation can be increased by the addition of a small quantity of baryta-water. The clear solution is then neutralised with hydrochloric acid and evaporated to the point of crystallisation. On the large scale the salt is easily prepared from heavy-spar. For this purpose 100 parts of the finely-powdered mineral are mixed with from 35 to 50 parts of carbon, from 15 to 25 parts of limestone and from 40 to 60 parts of calcium chloride. This mixture is heated in a reverberatory furnace and the mass lixiviated with water when insoluble calcium sulphide remains behind and the barium dissolves as chloride.

Barium chloride crystallises with two molecules of water in colourless rhombic tables (Fig. 113), which do not undergo any

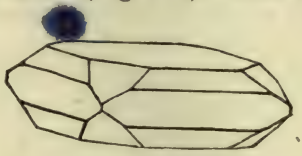


Fig. 113.

alteration in the air and have a specific gravity of 3·05. 100 parts of water dissolve:—

At	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	104°
$BaCl_2$	33·3	35·7	38·2	40·8	43·6	46·4	49·4	52·4	55·6	58·8	60·3.

Barium chloride is less soluble in dilute hydrochloric acid than it is in water. It is almost insoluble in the concentrated acid and also but slightly soluble in strong nitric acid and for this reason these acids precipitate concentrated solutions of a barium salt. Absolute alcohol does not dissolve barium chloride but dilute alcohol dissolves a small quantity, which increases in proportion to the amount of water present.

Crystallised barium chloride loses its water at a temperature of 113° forming a white powder, which melts at 847° and on cooling solidifies to a translucent mass. On exposure to the air the chloride in a state of fusion parts with a small quantity of chlorine, baryta being formed. Hence the fused salt usually has an alkaline reaction. When heated in a current of steam it emits hydrochloric acid at a temperature below its fusing

point. Barium chloride has an unpleasant bitter taste and acts as a powerful poison. The chief use of barium chloride is for the preparation of the artificial sulphate or *permanent white*. It has also been successfully employed for the prevention of incrustation in steam boilers when permanently hard waters are used. All the gypsum contained in solution is decomposed by barium chloride, whilst any calcium carbonate present in solution may be subsequently precipitated by milk of lime. The water thus softened forms no incrustation.

Barium Chlorate, $Ba(ClO_3)_2$, is obtained by adding barium chloride to a solution of sodium chlorate, double decomposition taking place:

$$2NaClO_3 + BaCl_2 = Ba(ClO_3)_2 + 2NaCl.$$

The solution on concentration deposits sodium chloride, which is fished out; the remaining solution is then evaporated and the barium chlorate purified by recrystallisation. It crystallises with one molecule of water in monosymmetric prisms which readily dissolve in water and alcohol, the latter solution burning with a characteristic green flame. If a drop of sulphuric acid be brought on to a mixture of the salt and powdered sugar it takes fire and burns with a bright green flame, and if the chlorate in a state of fusion and strongly heated, be plunged into an atmosphere of coal-gas combustion also takes place, the oxygen of the chlorate combining with the carbon and hydrogen of the coal-gas. It is largely used for pyrotechnic purposes.

Barium Iodate, $Ba(IO_3)_2$.—This salt is employed for the preparation of iodic acid. It is obtained as a white granular precipitate by adding potassium iodate to barium chloride (vol. i. p. 333). Barium iodate dissolves in 3,000 parts of cold and 600 parts of boiling water. It also dissolves in hot nitric acid from which solution it crystallises, on cooling, with one molecule of water in bright glittering monosymmetric prisms which are isomorphous with those of the chlorate and are decomposed by hydrochloric acid with evolution of chlorine.

Barium and Sulphur.

225 *Barium Monosulphide*, BaS, is obtained when sulphuretted hydrogen is passed over heated baryta as long as water is formed. On the large scale it is prepared by roasting 20 parts of slack

or pitch with 100 parts of heavy-spar. In order to assist the evolution of the carbon dioxide sawdust may be added to the mixture.

Pure barium sulphide is a white powder which decomposes in contact with water into barium hydroxide and barium hydrosulphide:

$$2BaS + 2H_2O = Ba(SH)_2 + Ba(OH)_2.$$

When a solution of 5 parts of the sulphide is boiled with 1 part of sulphur and the solution is allowed to evaporate in a vacuum, colourless transparent six-sided tables of $BaS + 6H_2O$ or possibly $BaSH(OH) + 5H_2O$ are deposited. When these crystals are treated with a small quantity of water, barium hydrosulphide dissolves and barium hydroxide remains behind.

Barium Hydrosulphide, $Ba(SH)_2$, is prepared by saturating water with barium hydroxide in an atmosphere of hydrogen at 100° and passing sulphuretted hydrogen free from oxygen through the solution heated to 60–70° for several days.[1] It crystallises with 4 molecules of water in aggregates of colourless spear-shaped needles, which dissolve in water and lose sulphuretted hydrogen readily when heated, so long as water is also driven off, the sulphur then remaining only being given off at a red-heat.

Barium Tetrasulphide, BaS_4, is obtained by boiling aqueous solutions of the sulphide or hydrosulphide with sulphur, and forms red crystals, containing according to Schöne 1 molecule, and according to Veley, 2 molecules of water. It dissolves in water forming a deep red solution. A *barium trisulphide* and *pentasulphide* have also been described, but their existence is doubtful.

Bononian Phosphorus.—The Bononian phosphorus which has been already mentioned (p. 453) is best prepared by heating 5 parts of precipitated barium sulphate together with one part of powdered charcoal over an ordinary gas flame for 30 minutes, and then igniting it more strongly over a gas blowpipe for ten minutes. Whilst hot the mass must be filled into glass tubes and the tubes sealed. After exposure to sunlight or to the light of burning magnesium wire this mass phosphoresces in the dark with a bright orange-coloured light. Strontium sulphate treated in the same way yields a mass which emits a faint yellowish-green light. If, however, the sulphide of strontium be ignited in a

[1] Veley, *Journ. Chem. Soc.* 1886, i. 369.

current of hydrogen gas, a body is obtained which phosphoresces with a green, blue, violet, or red light. If on the other hand the carbonate of strontium be ignited with sulphur, a mass is obtained which gives a blue or emerald green fluorescence. In this respect calcium salts do not act so satisfactorily as those of barium and strontium. According to Thomson an addition of 2 per cent. of manganese dioxide to calcium sulphide changes the phosphorescence from green to orange.

226 *Barium Sulphate*, $BaSO_4$, is by far the commonest and most widely distributed of the barium compounds, and occurs as heavy-spar, which crystallises in the rhombic system, Figs. 114 to 116. If anhydrous baryta be brought into contact with fuming sulphuric acid, or even with sulphuric acid which contains a small quantity of water, combination takes place with such rapidity

FIG. 114.

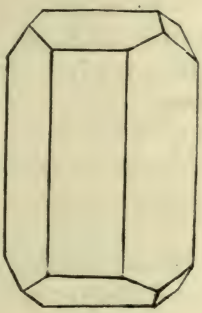


FIG. 115.

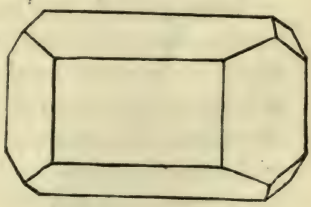


FIG. 116.

that the mass becomes incandescent. On the other hand, pure sulphuric acid which has the exact composition, H_2SO_4, does not act upon baryta, but if the mixture be touched in one place with a hot iron or with a moistened glass-rod, combination begins and is at once propagated throughout the mass (Kuhlman). Sulphuric acid and its salts precipitate the sulphate from a solution of a soluble barium salt in the form of a crystalline powder. The pure mineral heavy-spar has a specific gravity of 4·486 (H. Rose), the precipitated salt at 4° having a specific gravity of 4·53 (Schröder). This salt is almost insoluble in water, 1 litre dissolving only 0·0026 gram. at 18°. It is somewhat more soluble in dilute acids. If a salt of barium be heated with concentrated sulphuric acid, the sulphate dissolves to a certain extent and separates out on cooling in crystals having the composition $H_2SO_4 + BaSO_4$, and if this acid solu-

tion be exposed to moist air bright silky needles are formed having the composition $H_2SO_4 + BaSO_4 + 2H_2O$.

The crude heavy-spar is prepared for use as a paint, either alone or along with white lead, by being finely ground, treated with sulphuric acid to remove salts of iron, washed and dried. Artificial barium sulphate is also manufactured on a large scale and is known as *permanent white*, or *blanc fixé*. This preparation is largely used as a pigment and is much to be preferred for this purpose to the finely ground mineral, inasmuch as the latter, with its denser structure, is transparent and has but little "body" or covering power. In order to prevent the formation of finely divided crystals a solution of barium chloride having a specific gravity of 1·19 is precipitated in the cold with dilute sulphuric acid having a specific gravity of 1·245. The precipitate is washed with cold water and sent to market in the moist state. In addition to its value as a paint, blanc fixé is largely used for giving weight to cards and paper.

Barium Disulphate, BaS_2O_7.—If powdered barium sulphate be intimately mixed with fuming sulphuric acid it dissolves, forming a syrup, which on heating to 150° deposits the disulphate in glistening granular crystals which do not melt on heating and decompose at a dull red-heat.

Barium Dithionate, $BaS_2O_6 + 2H_2O$.—This salt is prepared by decomposing the corresponding manganese salt with barium sulphide. On allowing the solution to evaporate in a warm place glittering rhombic crystals of the salt are deposited. It dissolves at 18° in 4·04, and at 100° in 1·1 parts of water. On heating it is converted without change of form into barium sulphate.

Barium Persulphate, BaS_2O_8, is obtained by the action of barium hydroxide on ammonium persulphate, and crystallises in monosymmetric prisms which are readily soluble in water, and gradually decompose on keeping with formation of barium sulphate.

Barium and Nitrogen.

227 *Barium Nitride*, Ba_3N_2, is obtained by passing nitrogen over barium amalgam heated to redness, and forms a brown mass having a semi-metallic lustre, or sometimes yellowish acicular crystals. It is decomposed by water with evolution of hydrogen, ammonia and barium hydroxide remaining in solution, and

yields barium cyanide when heated in a current of carbonic oxide.[1] *Barium azoimide*, $Ba(N_3)_2$, obtained from ammonium nitride solution by boiling with baryta, forms hard lustrous crystals which explode on heating.

Barium Nitrate, $Ba(NO_3)_2$.—This salt is prepared on the large scale either by decomposing the carbonate or sulphide by dilute nitric acid, or by mixing hot saturated solutions of sodium nitrate and barium chloride. On cooling, the larger portion of the nitrate of barium crystallises out, and the remaining portion is obtained by evaporating the mother liquors. Barium nitrate crystallises in combinations of the cube and octahedron, and in other more complicated forms of the regular system (Lewis). Its specific gravity is 3·2; it possesses an acrid taste and melts at a temperature of 597° (Carnelley). 100 parts of water dissolve at

	0°	10°	20°	30°	40°	50°
$Ba(NO_3)_2$	5·2	7·0	9·2	11·6	14·2	17·1

	60°	70°	80°	90°	100°	102°
$Ba(NO_3)_2$	20·3	23·6	27·0	30·6	32·2	34·8

The salt is insoluble in concentrated nitric acid and in absolute alcohol and dissolves only sparingly in these liquids diluted with water. Barium nitrate is largely used for pyrotechnic purposes, especially for the preparation of green fire, and for the manufacture of an explosive powder known as *saxifragin*, which consists of a mixture of 76 parts of nitrate of barium, 22 parts of carbon, and 2 parts of nitre.

Barium and Carbon.

228 *Barium Carbide*, BaC_2.—This substance is obtained by heating baryta with charcoal in an electric furnace, and closely resembles the corresponding calcium compound.

Barium Carbonate, $BaCO_3$.—Barium carbonate occurs in nature as witherite. This mineral was discovered at Leadhills in Scotland by Withering in the year 1783. It crystallises in rhombic prisms and pyramids, is isomorphous with arragonite, and is chiefly found in England, one of its most celebrated localities being Fallowfield in Northumberland. It also occurs in Silesia, Hungary, Styria, Russia, Chili, and other places.

[1] Maquenne, *Compt. Rend.* 1892, **114**, 25, 220.

Alstonite $(BaCa)CO_3$ is isomorphous with witherite, and contains the two metals in varying proportions. Baryto-calcite, on the other hand, has the formulæ $BaCO_3 + CaCO_3$, and crystallises in the monosymmetric system.

Artificial barium carbonate is a dense white powder obtained when a solution of chloride of barium is poured into an excess of a hot solution of ammonium carbonate. One litre of water dissolves only 0·024 gram of barium carbonate at 18°, but it is more readily soluble in water containing carbonic acid. The artificial salt is employed in chemical analysis, and powdered witherite in the preparation of other barium salts and as a rat bane.

Silicates of Barium.—It has been already stated that many of these salts occur as crystalline minerals. Barium silicate is also a constituent of baryta-glass, a flint-glass in which the lead has been replaced by barium. This will be described under Glass Manufacture.

Detection and Estimation of Barium.

229 The non-luminous gas-flame is coloured a yellowish-green tint when any volatile barium compound is brought into it. The barium compounds yield the most complicated of the spectra of the alkalis and alkaline earths. The spectrum is, however, at once distinguished by the green lines Ba α and Ba β which are by far the most distinct, appearing the first and continuing during the whole of the experiment. Ba γ is not nearly so distinct, but is still a well-marked and peculiar line. As the spectrum of the barium compounds is more extended than the spectra of the compounds of the other metals, the reaction is not observed with so great a degree of delicacy, but it appears from Bunsen's experiments that about $\frac{1}{1000}$ of a milligram of barium salt may be detected with the greatest certainty. The chloride, bromide, iodide, and fluoride of barium, as well as the hydrated oxide, the sulphate, and carbonate, show the reaction best. It may be obtained by simply heating any of these salts in the flame. Silicates containing barium which are decomposed by hydrochloric acid give the reaction, if a drop of hydrochloric acid be added to them before they are brought into the flame. Baryta-harmotome, treated in this way, gives the lines Ca α and Ca β, together with the bands Ba α and Ba β. Com-

pounds of barium with fixed acids, giving no reaction either when alone or after addition of hydrochloric acid, should be fused with carbonate of sodium as described under strontium, and the carbonate of barium thus obtained examined. If barium and strontium occur in small quantities together with large amounts of calcium, the carbonates obtained by fusion are dissolved in nitric acid and the dry salt extracted with alcohol; the residue contains only barium and strontium, both of which can almost always be detected. To test for very small traces of strontium or barium, the residual nitrates are converted into chlorides by ignition with sal-ammoniac, and the chloride of strontium is extracted by alcohol. Unless one or more of the bodies to be detected is present in very small quantities, the methods of separation just described are quite unnecessary.

Soluble barium salts are distinguished from those of strontium and calcium, inasmuch as they are *immediately* precipitated by a solution of calcium sulphate. The qualitative separation of barium from strontium and calcium is usually effected by the addition of potassium chromate to a solution of the mixed salts containing acetic acid, barium chromate being precipitated. Barium and strontium may be separated by treating the mixed chlorides with absolute alcohol, or preferably by the action of amyl alcohol on the mixed bromides,[1] the barium salt being almost insoluble in both solvents. For quantitative estimation barium is almost always weighed as the sulphate, and in some special cases as the carbonate.

Atomic Weight of Barium.—The atomic weight of barium was determined by Marignac from the quantity of silver required to exactly precipitate a known weight of crystallised barium chloride, and also from the weight of barium sulphate obtained from the same salt, the number obtained being 136·15 (O = 15·88). Recently Richards[2] has redetermined the atomic weight by ascertaining the equivalent of both barium chloride and bromide to silver and silver chloride or bromide, and the results, which agree very closely, give the average number Ba = 136·41, when O = 15·88.

[1] Browning, *Amer. J. Sci.* 1893, **44**, 459.
[2] *Zeit. Anorg. Chem.* 1892, **3**, 441; 1893, **6**, 89.

THE MAGNESIUM GROUP.

230 The elements of this sub-group differ from the metals of the alkaline earths more especially in the properties of the metals themselves, which are much more readily obtained in the free state, and only undergo at most a slight superficial oxidation in the air at the ordinary temperature. At higher temperatures they combine with oxygen forming the oxide corresponding to the divalent series of salts, and magnesium and zinc slowly decompose water at the boiling point. They are colourless and ductile metals, the melting and boiling points of which decrease with increasing atomic weight, mercury being a liquid at the ordinary temperature, whilst it solidifies at a low temperature to a malleable solid. Most of the salts closely resemble the corresponding salts of the alkaline earth-metals, except that they exhibit a greater tendency to form basic salts, and that the sulphates are readily soluble in water, and yield crystalline double salts. Mercuric sulphate forms an exception, as it is converted by water into an insoluble basic salt and a soluble acid salt, and mercury also differs from the other metals inasmuch as it forms a monovalent series of salts in addition to the divalent series. Some of the magnesium and zinc salts combine with ammonia forming derivatives analogous to the ammoniacal copper compounds, and mercury yields a large series of derivatives, which appear to consist of simple or double salts of *dimercurammonium hydroxide*, NHg_2OH.

BERYLLIUM OR GLUCINUM, Be = 8·99.

231 Vauquelin in 1798 was the first to detect the existence of the oxide of this metal in beryl, this mineral having formerly been regarded as a compound of silica with lime or alumina. The earth contained in beryl was shown by Vauquelin to be a distinct body, differing from both lime and alumina, inasmuch as it formed a soluble sulphate which was incapable of uniting with potassium sulphate to form an alum. Haüy had previously observed that emerald was mineralogically identical with beryl, and on examining the former mineral Vauquelin found that it likewise contained the new earth. He did not give any special name to this new earth, but the editors of the

Annales de Chimie gave it the name of glucina from γλυκύς sweet, because its salts possessed a peculiar sweet taste. As, however, there are other salts which possess the same property, the name beryllia, derived from the mineral, was given to it by the German chemists.

Beryllium occurs in many minerals, especially in beryl $Be_3Al_2Si_6O_{18} = 3BeO,Al_2O_3,6SiO_2$. Beryl crystallises in hexagonal prisms, Figs. 117, 118, and 119, which usually have a green colour, colourless beryl being seldom met with. The transparent green-coloured varieties of beryl are known as emerald, those possessing a bluish-green tint being termed aquamarine. Beryl occurs also of a blue, yellow, grey, and rose-red tint. When the mineral is transparent it is termed precious beryl; when translucent or opaque it is known as common beryl. Beryllium

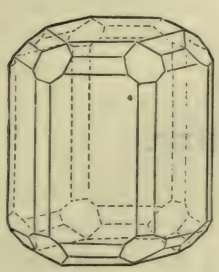


Fig. 117.

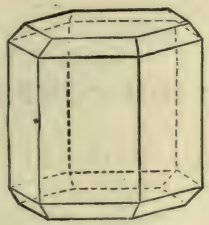


Fig. 118.

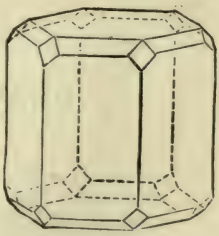


Fig. 119.

also occurs in leucophane $Na_2(CaBe)_5Si_5O_{15}F_2$; in phenacite, Be_2SiO_4; euclase, $H_2Be_2Al_2Si_2O_{10} = H_2O,2BeO,Al_2O_3,2SiO_2$; and chrysoberyl, BeO,Al_2O_3, as well as in other minerals.

Metallic Beryllium was first obtained by Wöhler in the year 1828 by fusing the chloride with potassium. Prepared in this way beryllium is a dark grey powder, which under the burnisher, assumes a bright metallic lustre.[1]

Debray first obtained the metal in a coherent state by placing in a glass tube two or more boats made of a mixture of clay and lime, the first containing beryllium chloride and the others metallic sodium. The air having been replaced by dry hydrogen, the boats were heated, by which means the beryllium chloride was vaporised and then reduced by the melted sodium. Later Nilson and Pettersson[2] prepared it by heating potassium beryllium fluoride with the calculated quantity of sodium in a

[1] *Ann. Chim. Phys.* 1855 (3), **44**, 5. [2] *Wied. Ann.* 1878, **4**, 554.

steel crucible. The metal has a specific gravity of 1·64, and a specific heat of 0·4079 (Nilson and Pettersson), giving an atomic heat of 3·7 (see p. 19). It possesses a bright silver-white colour, melts at a lower temperature than silver, and when heated before the blowpipe becomes covered with a film of oxide which prevents further oxidation. In the finely powdered state, on the other hand, it takes fire when heated in the air and burns with great brilliancy. The powdered metal dissolves in dilute acids: the compact form is readily soluble in dilute hydrochloric acid, but dilute sulphuric acid dissolves it only when warm, whilst concentrated nitric acid does not attack it in the cold, and on heating does so only slowly. The metal does not decompose water even at a red heat (Debray). Ammonia does not act either on the powder or on the compact metal, but both forms dissolve readily in caustic potash with evolution of hydrogen.

BERYLLIUM COMPOUNDS.

Beryllium and Oxygen.

232 *Beryllium Oxide, Beryllia,* or *Glucina,* BeO.—To obtain this earth from beryl the latter is fused with twice its weight of potassium carbonate and the melt treated with sulphuric acid; the excess of acid is evaporated off, water added, the silica removed by filtration and the solution concentrated. Almost the whole of the aluminium separates out on cooling as alum, and the mother liquor then contains chiefly the sulphates of beryllium and iron with small quantities of alum. To separate the beryllium advantage is taken of the solubility of beryllium hydroxide and carbonate in an excess of ammonium carbonate solution, the iron and alumina being left for the most part undissolved. In carrying out the separation the mother liquor is poured into a hot concentrated solution of ammonium carbonate, the liquid allowed to stand for several days, and the precipitated iron and aluminium salts filtered off. The filtrate on boiling deposits a basic beryllium carbonate together with a little ferric oxide.[1]

To prepare pure beryllia from this precipitate, it is re-

[1] Joy, *Amer. J. Sci.* (2), **36**, 83.

dissolved in ammonium carbonate solution, and a strong current of steam blown through the liquid, which precipitates the beryllia; this process is repeated several times, and the final precipitate is dissolved in hydrochloric acid, precipitated with ammonia, washed and dried.[1] According to Krüss[2] it then still contains a small quantity of impurity, which is removed by redissolving in ammonium carbonate solution, adding a little ammonium sulphide, and allowing it to stand for several days. A slight black precipitate is formed, and the filtered solution yields pure beryllia.

According to Gibson the best method of preparing beryllia from beryl is as follows:—Coarsely powdered beryl is heated with 6 parts of ammonium hydrogen fluoride for 10—12 hours at a heat not exceeding dull redness. The aluminium is thus almost completely converted into insoluble aluminium fluoride, and the residue on treatment with water yields a solution containing chiefly beryllium and iron fluorides. This is evaporated to dryness, and heated with strong sulphuric acid until the ferric sulphate formed commences to decompose, fluorine and silicon being thus completely removed. The solution obtained on adding water is boiled with nitric acid to oxidise the iron to the ferric state, and the filtered liquid poured into an excess of concentrated ammonium carbonate solution. The bulk of the iron separates on addition of an equal volume of hot water, and the filtrate is then mixed with an excess of mercuric chloride and precipitated with ammonium sulphide, the whole of the iron coming down together with the mercuric sulphide, whereas it is only partially precipitated if no mercury be first added. The filtered solution is boiled to precipitate the basic beryllium carbonate, which on ignition yields pure beryllia, any traces of ammonium and mercury salts being volatilised with the carbon dioxide.[3]

To prepare beryllia from leucophane, the latter, after separation from admixed tourmaline, is heated with sulphuric acid to remove fluorine, the excess of acid boiled off, the residue boiled with water, and the filtered extract added to an excess of ammonium carbonate solution. After ten days the solution is filtered and the filtrate boiled, and the precipitated crude basic beryllium carbonate treated in the manner already described.[4]

[1] Humpidge, *Proc. Roy. Soc.* 1886, **39**, 1. [2] *Ber.* 1890, **23**, 727.
[3] *Journ. Chem. Soc.* 1893, i. 909.
[4] Krüss and Moraht, *Ber.* 1890, **23**, 727.

Beryllia is a white amorphous powder having a specific gravity of 3·016, which when heated to the highest temperature of a wind furnace assumes the form of microscopic prisms resembling corundum (Rose). It may be easily obtained in this form by the ignition of a mixture of beryllium and potassium sulphates (Debray). It is insoluble in water, and only dissolves in dilute acids when it has not been strongly ignited. Concentrated boiling sulphuric acid dissolves it easily, and if it be fused with an alkali, and the cold mass treated with water, the beryllia goes into solution.

Beryllium Hydroxide, $Be(OH)_2$.—This is thrown down as a gelatinous precipitate when a beryllium salt is precipitated with ammonia. On drying it forms a voluminous white powder which is converted into the oxide by ignition.

Salts of Beryllium.

233 *Beryllium Chloride*, $BeCl_2$, is obtained in the form of white needle-shaped crystals when a mixture of the oxide and sugar-charcoal is ignited in a current of dry chlorine gas. The specific gravity of its vapour is 2·72, corresponding to the formula $BeCl_2$.[1] It is deliquescent, and dissolves in water with evolution of heat. When the aqueous solution is allowed to evaporate over sulphuric acid, colourless crystals of the hydrated chloride, $BeCl_2 + 4H_2O$, separate out. Beryllium chloride forms double salts with platinum chloride, tin chloride, and mercuric chloride. Several basic chlorides have also been described; they are, however, not well defined.

Sulphates of Beryllium.—The normal salt, $BeSO_4 + 4H_2O$, crystallises from a hot saturated solution in quadratic pyramids which dissolve at the ordinary temperature in their own weight of water, possess a sweet taste, and effloresce on exposure to the air. When heated they first melt in their water of crystallisation, leaving the anhydrous salt on further heating, which decomposes at a red-heat, beryllia remaining behind. A salt containing 7 molecules of water separates out from an acid solution of the normal salt, in large monosymmetric crystals which retain 1 molecule of water of crystallisation even at 150°. According to Klatzko this salt is isomorphous with magnesium sulphate,

[1] Humpidge, *Proc. Roy. Soc.* 1885, **38**, 188; Nilson and Pettersson, *Ber.* 1884, **17**, 987.

$MgSO_4 + 7H_2O$; this, however, appears, according to Marignac, to be doubtful. Beryllium readily forms basic sulphates. These are obtained by boiling the normal sulphate with beryllium carbonate, and form gelatinous or gum-like masses.

Beryllium Nitrate, $Be(NO_3)_2 + 3H_2O$, crystallises with difficulty. It is extremely deliquescent, and is easily soluble in alcohol. When heated for twenty hours on the water-bath a thick mass is obtained, which is readily soluble in water. This consists of the basic salt, $Be(OH)NO_3 + H_2O$.

Beryllium Carbide, BeC_2, is obtained by heating beryllia with sugar charcoal, and a little oil, to a very high temperature in the electric furnace, and forms transparent yellowish-brown microscopic crystals, which are slowly decomposed by water and dilute acids with evolution of pure methane.[1]

Carbonates of Beryllium.—The normal carbonate, $BeCO_3 + 4H_2O$, is obtained by passing carbon dioxide for a considerable time through water containing the basic carbonate of beryllium in suspension. The solution is allowed to evaporate over sulphuric acid in an atmosphere of carbon dioxide. Crystals are then formed which readily decompose with evolution of carbon dioxide.

When a solution of a beryllium salt is added to an alkaline carbonate, or when a solution of the oxide in ammonium carbonate is boiled, a basic carbonate of varying composition separates out as a white powder.

Detection and Estimation of Beryllium.

2-4 The salts of this metal do not impart any tint to the non-luminous gas-flame. The beryllium spark-spectrum contains two characteristic bright lines in the blue, having a wave-length of 4,573 and 4,489 (Kirchhoff and Thalén). These lines are, however, not seen when the chloride is volatilised in the electric arc (Bunsen).

Beryllium may be readily separated from all other metals by the fact that its oxide is soluble in ammonium carbonate solution. In the process of analysis it is precipitated together with alumina, and it may be separated from this earth by treatment with ammonium carbonate. For quantitative estimation and for separation from alumina and ferric oxide the method pro-

[1] *Compt. Rend.* 1895, **121**, 496, 600.

posed by Joy may be employed. The precipitate is treated with ammonium carbonate, the filtrate boiled, and the precipitated basic carbonate of beryllium converted by ignition into the oxide, which is weighed.

The atomic weight of beryllium has been determined by Nilson and Pettersson [1] by analysis of the sulphate, and found to be 9·04 whilst Krüss and Moraht [2] by the same method find it to be 8·99 (O = 15·88).

MAGNESIUM, Mg = 24·2.

235 Nehemiah Grew, a London physician living in the seventeenth century and for some time secretary of the Royal Society, published in the year 1695 an account of a peculiar salt found in the well-known mineral spring at Epsom under the title "*De salis carthartici in aquis Ebshamensibus et alius contenti natura et usu.*" The medicinal value of this salt soon afterwards became widely celebrated, and the salt was known in England as Epsom-salts, and on the Continent as English-salt. The presence of the same substance was soon afterwards detected in other English mineral springs, and George and Francis Moult in the year 1700 established a large manufactory of the salt near London, obtaining it from a spring at Shooter's Hill. In 1710 Hoy discovered that the same salt could be obtained by crystallisation from the mother-liquors of sea-water after addition of green vitriol (ferrous sulphate). The same salt was subsequently shown to exist by Fr. Hoffmann in the Sedlitz mineral water. Another compound of magnesium having medicinal value was also discovered at the beginning of the eighteenth century by a Roman ecclesiastic and termed by him *magnesia alba*. Why this name was given to it in contrast to *magnesia nigra*—as black oxide of manganese was then called—is not known. The mode of preparation of this substance was for some years kept secret, until in the year 1707 Valentini, of Giessen, pointed out that magnesia alba could be obtained by boiling down the mother-liquors from the preparation of nitre and igniting the residual products. Shortly afterwards, in 1709, Slevogt, of Jena, prepared the same substance by the precipitation of saltpetre mother-liquors with a fixed alkali. The substance thus obtained

[1] *Ber.* 1880, **13**, 1451. [2] *Ber.* 1890, **23**, 2556.

was a mixture of calcium carbonate and magnesium carbonate in varying proportions, and hence its medicinal action was very variable, and a satisfactory discrimination between lime and magnesia was rendered more difficult. The distinction between these two earths was first clearly pointed out by Black in the year 1755. He showed that white magnesia was a compound of fixed air with a peculiar earth, which differed from lime in yielding a soluble sulphate. The properties of the new earth were subsequently more completely investigated by Bergman in 1775, but Black retained for it the name of magnesia. When Davy proved that this earth was the oxide of a metal, the name of *magnium* was given by him to the metal, the name *magnesium* or *manganesium* being at that time used to designate the metal contained in pyrolusite. This confusion was put an end to by the general adoption of the name magnesium for the metal contained in magnesia alba, and of manganese for that contained in pyrolusite.

Magnesium is a metal widely distributed in nature. It is found as magnesite, $MgCO_3$; dolomite, $(MgCa)CO_3$; kieserite $MgSO_4 + H_2O$; kainite, $MgSO_4 + KCl + 6H_2O$; carnallite, $MgCl_2 + KCl + 6H_2O$; spinelle, $MgOAl_2O_3$; asbestos $(MgCa)SiO_3$; talc, $H_2Mg_3Si_4O_{12}$; meerschaum, $H_2Mg_2Si_3O_9 + H_2O$, and as the chief constituent of many silicates such as augite, olivine, tourmaline, and serpentine, while it is contained in smaller quantities in most of the other silicates.

Magnesium sulphate, $MgSO_4 + 7H_2O$, is a chief constituent of certain saline springs, whilst the chloride, $MgCl_2$, occurs in salterns and in sea-water. Magnesium is also found in the animal and vegetable worlds. The bones of animals and the seeds of the cereals contain small quantities of magnesium phosphate, and ammonium magnesium phosphate separates out from the urine on standing, thus giving rise to many urinary deposits as well as to gravel and stone. The same salt likewise occurs in guano.

236 *Preparation of Metallic Magnesium.*—Davy was the first to prepare metallic magnesium, but he did not obtain it in the pure state. It was first obtained as a coherent metal by Bussy,[1] who fused the anhydrous chloride of magnesium with potassium. Bunsen afterwards obtained it by the electrolysis of magnesium chloride, which is for this purpose fused in a porcelain crucible,[2] (Fig. 120): the carbon of the negative pole

[1] *Journale de Chimie Medicale Ann.* 1830, 141. [2] *Annalen*, 1852, **82**, 137.

is cut so as to form pockets, as shown in Fig. 121, inside which the metal is deposited: unless this precaution be taken, the metal, being lighter than the fused chloride, rises to the surface and burns. As it is difficult to prepare the pure chloride, Matthiessen employed a mixture of the chlorides of potassium and magnesium in nearly equal proportions, namely, in the ratio of 3 molecules of potassium chloride to 4 of magnesium chloride.[1]

Magnesium is also prepared according to the method proposed by Caron and Deville.[2] For this purpose a mixture of 600 grams of fused chloride of magnesium, 480 grams of finely-powdered fluor-spar, and 230 grams of sodium in small pieces is thrown into a red-hot crucible, which is then closed with the cover. After a short time a violent reaction takes place, and as soon as

FIG. 120.

FIG. 121.

this is complete the contents of the crucible are stirred round with an iron rod in order to unite the small globules of metal into larger masses. To avoid the somewhat troublesome preparation of the anhydrous chloride, Wöhler suggested the use of the fused double chloride of magnesium and sodium. Sonstadt, in place of this, employed a mixture of potassium chloride and magnesium chloride, which may be also obtained by fusing the mineral carnallite. Care however must be taken that no kieserite is present, otherwise explosions may occur.

The manufacture of magnesium on the large scale was first effected by Sonstadt and Mellor. The process is essentially that of Caron and Deville, an important improvement being the distillation of the crude metal, as this usually contains carbon, silicon, and nitrogen. The fact that magnesium can be readily distilled was indeed discovered by Deville and Caron, but

[1] *Journ. Chem. Soc.* 1856, 107.
[2] *Ann. Chim. Phys.* 1863 [3], **67**, 347.

first technically employed by Sonstadt. For this purpose the crude magnesium is placed in an iron crucible having an iron tube passing through from the bottom to within an inch of the lid. The crucible is filled with the crude metal to the level of the mouth of the tube, the lid carefully screwed and luted down, and the air displaced by a current of hydrogen or coal-gas. As the crucible becomes heated the magnesium distils over, passing through the upright tube into a box placed below, where, on the completion of the operation, it is found in the form of a coherent mass which is subsequently melted and cast into ingots or any other form that may be required. The metal is usually pressed when in a semi-fluid state into wire of varying thickness and of any required length, and this afterwards flattened into ribbon, in which form it usually occurs in commerce. Magnesium is now manufactured by the Magnesium Metal Company at Patricroft near Manchester, and also by the American Magnesium Company at Boston.

237 *Properties.*—Magnesium is a brilliant white metal, which melts at 632·7° (Heycock and Neville), boils at about 1100°, and has a specific gravity of 1·75, a granular crystalline fracture, and is sometimes obtained in hexagonal crystals isomorphous with those of cadmium and zinc. It preserves its lustre in dry air, but in moist air becomes covered with a film of oxide, and when a piece of ribbon is held in the flame of a candle it burns with an intensely white light. The heated metal readily decomposes steam, hydrogen being evolved and magnesia produced. The light from burning magnesium wire is rich in chemically active rays, so that it is possible to photograph by means of it. Bunsen and Roscoe have determined the actinic value of this light compared with that of the sun.[1] They showed that a burning surface of magnesium wire, which seen from a point at the sea's level has an apparent magnitude equal to that of the sun, effects, at that point, the same chemical action as the sun would do if shining from a cloudless sky at the height of 9° 53′ above the horizon. On comparing the visible brightness of these two sources of light it was found that the brightness of the sun's disc as measured by the eye is 524·7 times as great as that of burning magnesium when the sun's zenith-distance is 67° 22′, whilst at the same zenith-distance the sun's *chemical brightness* was only 36·6 times as great. Hence the value of this light as a source of chemically

[1] *Phil. Trans.* 1859, 920.

active rays for photographic purposes becomes at once apparent. The application of magnesium as a source of light has become of technical importance. A burning magnesium wire of the thickness of 0·297 mm. evolves as much light as 74 stearin candles of which five go to the pound. If this light lasted one minute 0·987 m. of wire weighing 0·120 gram. would be burnt. In order to produce a light equal to 74 candles burning for ten hours whereby 20 lbs. of stearin is consumed, 72·2 grams or $2\frac{1}{2}$ oz. of magnesium would be needed. The light from burning magnesium has been employed for signalling, and for military and naval purposes, and it is especially employed in pyrotechny.

Metallic magnesium combines with nitrogen on heating forming the nitride, and is also made use of in chemical analysis, and in toxicological investigations, where, as it is perfectly free from arsenic, it may be used with advantage in Marsh's apparatus in the place of zinc. It is also used in the estimation of nitrates and nitrites in drinking water, and in other cases, as a reducing agent. In the form of powder it reduces most metals from their oxides when heated with the latter, and is used for the preparation of several elements such as silicon and boron.[1] Magnesium also burns readily in carbon dioxide, carbon being deposited.

MAGNESIUM COMPOUNDS.

Magnesium and Oxygen.

238 *Magnesium Oxide or Magnesia,* MgO.—This substance is formed when the metal burns in the air, and is also produced by the ignition of the magnesium salt of any volatile oxy-acid. It is prepared on the large scale by igniting the carbonate, magnesia alba, and forms a very fine light powder, known as *magnesia usta* or *calcined magnesia.* It is almost insoluble in water, 1 part dissolving in 55,000 parts of both hot and cold water (Fresenius). It is tasteless, but in the moist state turns red litmus-paper blue. When heated in an electrical furnace at 2,500° it forms transparent crystals, and at a higher temperature melts and finally volatilises, though less readily than lime. When magnesia is ignited in a current of

[1] Winkler, *Ber.* 1890, **23**, 44, 120.

hydrochloric acid it is obtained in the form of regular cubes and octohedra, and if a mixture of magnesia and ferric oxide be treated in this way black octohedra of magnoferrite, MgO,Fe_2O_3, are formed together with those of MgO containing a little ferric oxide; these are of a yellow colour, identical with periclase, a mineral found at Monte Somma, near Naples.

Magnesia is employed as a medicine, as a refractory lining in furnaces and for the manufacture of crucibles, and in certain processes for the regeneration of chlorine from ammonium chloride.

Magnesium Hydroxide, $Mg(OH)_2$, is obtained as a white precipitate when aqueous potassium or sodium hydroxide is added to a solution of a magnesium salt, and occurs in nature as the mineral brucite, which is found imbedded in serpentine with other magnesium minerals. It is almost insoluble in water, but the solubility is greatly increased by the presence of ammonium salts, and hence the hydroxide is not precipitated from solutions of magnesium salts by ammonia in presence of ammonium salts. In like manner magnesium carbonate is not precipitated in presence of ammonium salts, soluble double carbonates of magnesium and ammonium being formed (p. 485).

Magnesium and the Halogens.

239 *Magnesium Fluoride*, MgF_2, occurs as the mineral sellaïte in colourless quadratic crystals, found at Montiers in Savoy. When pure magnesia is evaporated with an excess of aqueous hydrofluoric acid to dryness, this same compound is obtained as an amorphous mass. When this is fused with common salt and the mass gradually cooled, it is deposited in crystals which, after washing with water, exhibit the same form as sellaïte (Cossa).

Magnesium Chloride, $MgCl_2$, is contained in sea-water, in many brine-springs, and in various salt-beds, and is at present prepared in large quantities at Stassfurt. It is very soluble in water, 100 parts of water dissolving at the ordinary temperature about 130 parts, and at the boiling point 366 parts of the salt. The hot concentrated solution deposits on cooling needles or prisms of the deliquescent hydrated salt, $MgCl_2 + 6H_2O$.

The hydrated salt is decomposed on heating, water and hydrochloric acid being given off and magnesia remaining. In

order to prepare the anhydrous salt, sal-ammoniac is added to the solution; this is then evaporated to dryness, and the residue carefully heated until it is anhydrous, and afterwards ignited in a platinum crucible; it may also be obtained in the anhydrous form by evaporating the solution in a current of hydrochloric acid gas (Hempel). The clear fused mass solidifies on cooling, forming a laminated crystalline solid which dissolves in water with evolution of heat. It possesses a bitter saline taste, and is now largely used for the purpose of dressing cotton goods. Magnesium chloride forms crystalline double salts with other chlorides, especially with those of the alkaline earths. Of these the following are the most important:

Potassium Magnesium Chloride or Carnallite, $MgCl_2, KCl + 6H_2O$.—This compound crystallises in rhombic prisms which deliquesce on exposure to the air, leaving a residue of potassium chloride.

Ammonium Magnesium Chloride, $MgCl_2,NH_4Cl + 6H_2O$, is deposited from solution in small rhombic crystals which dissolve in six parts of water.

Calcium Magnesium Chloride or Tachhydrite, $2MgCl_2, CaCl_2 + 12H_2O$, occurs at Stassfurt in yellowish rounded masses which deliquesce on exposure to the air.

Oxychlorides of Magnesium.—If strongly ignited magnesia be brought into contact with a concentrated solution of the chloride, the mixture after standing for some hours solidifies to a mass so hard that it is capable of being polished (Sorel). A mass of this kind which had been exposed for six months to the air gave results on analysis which render it probable that it is a mixture of magnesium carbonate and the compound

$MgCl_2,5MgO + 17H_2O$, or $2Mg\left\{\begin{matrix}Cl\\OH\end{matrix}\right. + 4Mg(OH)_2 + 12H_2O$.

This substance loses water on heating, but does not give off hydrochloric acid, and chloride of magnesium may be withdrawn from it by repeatedly boiling with water, leaving a residue of magnesium hydroxide as a hard non-crystalline mass resembling brucite.[1] If a solution of magnesium sulphate to which ammonia and sal-ammoniac have been added (a mixture frequently used in the laboratory) be allowed to stand for some time a crystalline precipitate having the composition $2Mg\left\{\begin{matrix}OH\\Cl\end{matrix}\right. + 4Mg(OH)_2 + 8H_2O$ is sometimes formed (J. Davis).

[1] Bender, *Annalen*, 1871, **159**, 341.

Magnesium Bromide, $MgBr_2$, occurs in sea-water and in many brine-springs. The anhydrous salt is obtained by heating magnesium in bromine vapour, or by leading bromine vapour over an ignited mixture of magnesia and sugar charcoal. It forms a white crystalline mass which hisses and evolves heat when brought into contact with water, and crystallises from a hot concentrated solution in needles, having the composition $MgBr_2 + 6H_2O$. On heating the crystals, hydrobromic acid is given off and magnesia is left behind.

Magnesium Iodide, MgI_2, is found together with the bromide in sea-water and brine-springs. It can be prepared by dissolving magnesia in hydriodic acid. On evaporation, hygroscopic crystals of a hydrated salt are deposited, which readily undergo decomposition with liberation of iodine.

Magnesium and Sulphur.

240 *Magnesium Sulphide*, MgS.—This substance is not formed in the wet way, but is obtained when a mixture of magnesium filings and sulphur is heated to dull redness in a current of sulphur vapour.[1] The product is a brown, coherent, hard, and brittle coke-like mass, mixed with a small quantity of magnesium oxide and some undecomposed metal. On exposure for some time to the air the difficultly fusible sulphide slowly tarnishes, and evolves sulphuretted hydrogen, and the granular and bright steel-grey fracture becomes dull and coated with a grey oxide. It is slightly soluble in water, yielding a straw-yellow solution, but on exposure to the light it deposits sulphur and becomes colourless. This solution doubtless contains magnesium hydrosulphide, $Mg(SH)_2$, which may also be obtained by passing sulphuretted hydrogen into water containing magnesia in suspension.[2] It is an extremely unstable compound, and on exposure to the air, or when heated, gives off sulphuretted hydrogen, leaving magnesia behind. A solution of this substance has been proposed as a source for sulphuretted hydrogen for laboratory purposes.

Magnesium Sulphate, $MgSO_4$, occurs in nature as *kieserite*, $MgSO_4 + H_2O$, and *Epsom salts*, $MgSO_4 + 7H_2O$. These two compounds can be readily distinguished by the action of water on

[1] Parkinson, *Journ. Chem. Soc.* 1867, 127.

[2] Berzelius, *Pogg. Ann.* 1825, **6**, 443.

them. Epsom salts are readily soluble in water, whilst kieserite is as difficultly soluble as gypsum. Kieserite occurs crystallised in rhombic prisms, but is more commonly found in granular masses which dissolve slowly when allowed to remain in contact with water, being gradually converted into Epsom salts. Epsom salts occur in many mineral-waters. The same compound is found as epsomite or hair-salt in silky fibres and fibrous crusts at Idria in Carniola, in the gypsum quarries of Montmartre near Paris, and in various other localities. The floors of the limestone caves in Kentucky, Tennessee, and Indiana are in many instances covered with minute crystals of epsomite mingled with earth. In the Mammoth cave in Kentucky it adheres in loose masses like snow balls (Dana).

The manufacture of magnesium sulphate from the upper layers of salt (*Abraumsalz*) at Stassfurt is carried out on the large scale. The crude kieserite is placed in sieves in water. The magnesium chloride and finely divided chloride of sodium dissolve whilst the kieserite falls through the meshes of the net in small powder, and larger pieces of rock-salt, anhydrite, and earthy impurities remain behind. This powder is then brought into conical wooden moulds in which it is allowed to remain, and in which it soon becomes a hard coherent mass, inasmuch as a portion of the salt combines with water to form the hepta-hydrate which binds together the remaining powder of the kieserite. This kieserite-stone is then dried and powdered, and contains 80 to 90 per cent. of magnesium sulphate, and from 1 to 2 per cent. of common salt. It is either brought into the market in this form or worked up into Epsom salts. Sulphate of magnesium was formerly produced in considerable quantity by treating either native magnesium carbonate or dolomite with sulphuric acid; the gypsum formed in the latter case, being much less soluble than magnesium sulphate, is easily separated from it. Formerly, also, dolomite was burnt, the lime dissolved out by crude pyroligneous acid, and the residual magnesia treated with sulphuric acid (Henry).

Magnesium sulphate crystallises from a hot concentrated solution in four-sided rhombic prisms shown in Fig. 122, containing seven molecules of water, and isomorphous with the corresponding sulphates of zinc and nickel. As a rule, the commercial salt occurs in the powdery form consisting of minute delicate needles obtained by quick crystallisation of a concentrated solution. The crystals are not efflorescent, but the commercial salt

sometimes becomes moist in contact with air in consequence of the presence of traces of magnesium chloride. The crystals possess an unpleasant saline bitter taste and have a specific gravity of 1·685 (Schiff). On heating, they melt in their water of crystallisation, and lose six molecules at 150°, the last molecule being termed by Graham *constitutional water*, because it is not driven off until a temperature of 200° is reached. The salt is freely soluble in water; according to Gay-Lussac 100 parts of water at 0° dissolve 25·76 parts of the anhydrous salt and an additional 0·47816 for every degree above this. Magnesium sulphate is insoluble in absolute alcohol.

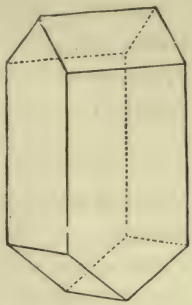


Fig. 122.

When a boiling and concentrated solution of magnesium sulphate is placed in a closed vessel it remains supersaturated when cold. Such a solution may stand for weeks or months without solidification, but milk-white crystals are sometimes deposited which contain six molecules of water, and, sometimes, monosymmetric tables with seven molecules of water are obtained. From this it is seen that Epsom salts is dimorphous; this is also shown by the fact that it crystallises as an isomorphous constituent with monosymmetric ferrous sulphate, $FeSO_4 + 7H_2O$. Epsom salts is largely used as a purgative, and, like the chloride, is employed as a dressing for cotton goods. It is also used in dyeing with aniline colours, as goods thus dyed are found to stand the action of soap better; this is probably due to the formation of an insoluble magnesia soap.

Magnesium sulphate forms a series of characteristic double salts with the sulphates of the alkali-metals. These have the general formula $MgSO_4 + M'_2SO_4 + 6H_2O$, and crystallise in well-developed monosymmetric prisms. When the anhydrous sulphate is dissolved in hot concentrated sulphuric acid the solution on standing deposits the compound $MgSO_4 + H_2SO_4$, in six-sided tables, which soon absorb moisture from the air and are thereby decomposed.[1]

[1] Schiff, *Annalen*, 1861, **118**, 365.

Magnesium and Nitrogen, Phosphorus and Arsenic.

241 *Magnesium Nitride*, Mg_3N_2.—Deville and Caron, when preparing magnesium, observed that the distilled metal sometimes appeared covered with small transparent needles,[1] which decomposed in moist air with formation of ammonia and magnesia, and therefore contained a nitride of magnesium. This compound was obtained in the amorphous state by Briegleb and Geuther,[2] by igniting magnesium in ammonia or in nitrogen gas. The nitride of magnesium thus prepared is a greenish-yellow amorphous mass, which when heated in dry oxygen gas is converted, with bright incandescence, into magnesia. On exposure to the air or when treated with water it is quickly decomposed into ammonia and magnesia, so much heat being evolved in the latter case that the water boils. When heated in a current of sulphuretted hydrogen gas, ammonium sulphide and magnesium sulphide are formed.

Magnesium Nitrate, $Mg(NO_3)_2$.—This salt occurs in the mother-liquors from the saltpetre manufacture, and in the surface water of towns, having been first detected by Berzelius in the well-water of Stockholm. It is prepared by dissolving magnesia alba in nitric acid. The hydrated salt, containing six molecules of water, crystallises from concentrated solutions in prisms and needles, which dissolve in half their weight of cold water and in nine parts of alcohol of specific gravity 0·84, but are less soluble in pure alcohol.

242 *Phosphates of Magnesium.—The Normal Orthophosphate*, $Mg_3(PO_4)_2$, occurs in small quantities in the seeds of the cereals and in bones. It is obtained in the form of a white precipitate when a solution of normal sodium orthophosphate is added to a solution of Epsom salts. One part of the salt dissolves in 5,000 parts of water. A phosphato-fluoride of magnesium having the formula $2Mg_3(PO_4)_2 + MgF_2$ occurs in nature as *wagnerite*.

Hydrogen Magnesium Orthophosphate, $HMgPO_4$, is obtained when a solution of Epsom salts is mixed with one of common sodium phosphate; on standing, hexagonal needles of the acid salt containing seven molecules of water are deposited. These dissolve in 322 parts of cold water. If this solution be heated it becomes milky owing to the separation of the insoluble normal

[1] *Ann. Chim. Phys.* 1863 [3], **67**, 348.

[2] *Annalen*, 1862, **123**, 228; see also Merz, *Ber.* 1891, **24**, 3940.

salt, a tetra-hydrogen phosphate, $H_4Mg(PO_4)_2$, remaining in solution. This latter compound has not been obtained in the pure state.

Magnesium Ammonium Orthophosphate, $Mg(NH_4)PO_4+6H_2O$. This salt, a frequent constituent of urinary calculi, was discovered by Fourcroy. It is produced in the putrefaction of urine, and large crystals of it have been found in some varieties of guano. It is formed when an ammoniacal solution of sal-ammoniac is mixed with a solution of magnesium sulphate, and a soluble orthophosphate then added. If the solution be dilute, the precipitate takes some time to form, and deposits in small crystals which attach themselves to the sides of the vessel, especially upon points presenting any roughness or inequality, as where the beaker-glass has been scratched. It separates in this way from extremely dilute solutions, affording a very delicate test either for magnesium or for phosphoric acid. According to Graham the best mode of obtaining it in distinct crystals is to mix 600 parts of hot water with four parts of strong ammonia; then add seven parts of crystallised sodium phosphate, two parts of sal-ammoniac and four parts of magnesium sulphate. The crystals which are thus deposited are transparent quadratic prisms. One part of the salt dissolves in 15,000 parts of water at 15° and in 44,000 parts of ammoniacal water, whilst in presence of sal-ammoniac it is somewhat more readily soluble. At 100° the salt gives off five molecules of water without loss of ammonia, and at a higher temperature the whole of the water and ammonia escapes, pyrophosphate of magnesium, $Mg_2P_2O_7$, remaining behind.

The Arsenates of Magnesium closely correspond to the phosphates.

Magnesium and Carbon and Silicon.

243 *Carbonates of Magnesium.—Normal Magnesium Carbonate*, $MgCO_3$, occurs in nature as magnesite, a mineral isomorphous with calc-spar. The same mineral frequently occurs in compact or granular masses, and is found in large quantities in various localities, especially in the island of Eubœa. The normal carbonate is also formed by the action of magnesium chloride on calcium carbonate (Marignac). It has a specific gravity of 3·056; it is not easily soluble in dilute acid, but dissolves in water saturated with carbon dioxide, being soluble in larger

quantity when the pressure to which the liquid is subjected is increased. According to Wagner[1] one part of magnesium carbonate dissolves at 5° in

761 parts of carbonic acid-water under a pressure of 1 atmosphere
134 „ „ „ „ 3 atmospheres
110 „ „ „ „ 5 „
76 „ „ „ „ 6 „

The solution has an alkaline reaction and a bitter taste. If it be placed in a partially closed flask at 50°, crystals of the hydrated carbonate, $MgCO_3 + 3H_2O$, are deposited from solution, whilst at a lower temperature tabular crystals containing five molecules of water separate out. When evaporated to dryness, the solution yields a crystalline powder which, examined under the microscope, is found to consist of crystals having the form of arragonite;[2] but if the solution be heated to 300° in a vessel closed by a porous stopper through which the carbonic acid can slowly escape, microscopic rhombohedra of the form of native magnesite are deposited.[3] Magnesium carbonate is, therefore, isodimorphous with calcium carbonate.

If a solution of Epsom salts be precipitated with an excess of sodium carbonate, and the precipitate boiled until it becomes crystalline, a basic carbonate having the composition

$$2MgCO_3, Mg(OH)_2 + 2H_2O$$

is thrown down in the form of small granular crystals. The *magnesia alba* of the shops is also a basic carbonate, which usually possesses the composition $3MgCO_3, Mg(OH)_2$, together with from two to three molecules of water, and is a very light powder (*magnesia alba levis*). This is obtained by precipitating a solution of Epsom salts or magnesium chloride with sodium carbonate. If the precipitation be carried on at the boiling temperature a much more dense precipitate is obtained (*magnesia alba ponderosa*).

Another method of preparation is that patented by Pattinson, which consists in igniting dolomite (a mixture of the carbonates of calcium and magnesium), and then treating it with water and carbon dioxide under pressure, when the carbonate of magnesium dissolves in the carbonic acid more readily than the

[1] *J. Pr. Chem.* 1867, **102**, 233.
[2] H. Rose, *Pogg. Ann.* 1837, **42**, 366.
[3] Sénarmont, *Ann. Chim. Phys.* 1850 [3], **30**, 129.

carbonate of calcium ; the solution of bicarbonate of magnesium which is formed is decanted from the insoluble carbonate of calcium and decomposed by a current of steam. The salt thus obtained is very white and of a loose texture.

The mineral termed *hydromagnesite*, possessing the same composition as magnesia alba, occurs in small white monosymmetric crystals.

Magnesia alba is almost insoluble in water. It dissolves, however, readily in solutions of ammoniacal salts, owing to the formation of ammonium carbonate and soluble double carbonates of magnesium and ammonium. For this reason ammonium carbonate does not precipitate a magnesium salt completely, and no precipitate occurs in the presence of sal-ammoniac.

Magnesium Silicide, Mg_2Si.—This compound was obtained by Wöhler as a by-product in the preparation of metallic magnesium, by fusing together a mixture of sodium, magnesium chloride and sodium silicofluoride, and was prepared by Geuther by heating alternate layers of fused and powdered sodium chloride, and a mixture of 2·5 parts of sodium chloride, 7 parts of sodium silicofluoride and 2·5 parts of magnesium to a high temperature in a Hessian crucible.[1] It is most readily obtained by heating 1 part of quartz sand and 1·5 parts of magnesium powder, and then forms a bluish half-fused mass,[2] but when obtained by Geuther's method, it forms crystals having a metallic lustre. It has probably the formula Mg_2Si, although Wöhler found the composition Mg_4Si_3 and Geuther Mg_5Si_3. This variation in the results is probably due to the fact that the product readily loses magnesium on ignition,[3] or the substances may be mixtures of Mg_2Si and MgSi. In favour of the latter view is the fact that when the silicide is treated with hydrochloric acid, spontaneously inflammable silicon hydride is evolved, and silicoformic anhydride formed (vol. i., p. 811), the decompositions being thus represented—

(1) $Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$.
(2) $2MgSi + 3H_2O + 4HCl = 2MgCl_2 + Si_2H_2O_3 + 4H_2$.

[1] *J. Pr. Chem.* 1865, **95**, 424.
[2] Gattermann, *Ber.* 1889, **22**, 186.
[3] Winkler, *Ber.* 1890, **23**, 2642.

Detection and Estimation of Magnesium.

244 Magnesium and its compounds do not impart any tint to the non-luminous gas-flame. The spark spectrum of magnesium is, however, very characteristic (Bunsen, Kirchhoff, Thalén), giving lines in the green coincident with Fraunhofer's *b*. The brightest of these lines is situated very close to an air-line, and for this reason it is better to observe the magnesium spark in an atmosphere of hydrogen, or in one of coal-gas, than in the air (Bunsen).

In the course of ordinary qualitative analysis, magnesium is obtained together with the alkali-metals, as it is not precipitated by carbonate of ammonium in presence of sal-ammoniac. The presence of magnesium is readily detected by the addition of sodium phosphate to a portion of the solution, as on standing for a short time a crystalline precipitate of $Mg(NH_4)PO_4 + 6H_2O$ is deposited. The formation of this precipitate is greatly accelerated by stirring the solution with a glass rod when the crystals are deposited where the rod has scratched the glass.

Magnesium is usually estimated by precipitation as magnesium ammonium phosphate by means of sodium phosphate in the presence of ammonia and ammonium chloride. The precipitate is washed with dilute ammonia in which it is less soluble than in pure water, and is then converted by ignition into the pyrophosphate, which is weighed. The quantitative separation of magnesium from the alkalis is accomplished by the method proposed by Berzelius. The solution which must contain the metals in the form of chlorides, as is indeed always the case in the analysis of silicates, &c., is evaporated to dryness, and the residue ignited in order to volatilise the ammoniacal salts. The fixed residue is then warmed with a small quantity of water, and a little finely divided oxide of mercury added, the mixture again evaporated to dryness on a water-bath, and the residue ignited in order to expel the mercuric chloride and excess of oxide. The residue contains the magnesium in the form of oxide, whilst the alkali-metals remain as chlorides, and are soluble in water. The undissolved magnesia after having been well washed is dissolved in hydrochloric acid, and precipitated as the ammonium magnesium phosphate.

Atomic Weight of Magnesium.—The atomic weight of magnesium has been very carefully determined by Marignac[1] by the analysis and synthesis of magnesium sulphate, the average number obtained being 24·20 (O = 15·88). Burton and Vorce,[2] by converting a known weight of pure magnesium into magnesia, obtained the number 24·10.

ZINC. Zn = 64·9.

245 The ancients were acquainted with the alloy of zinc and copper which we term brass, but they were not aware that it contained any other metal besides copper, and it was only after some time that a more accurate examination of brass and the ores which were employed for its production led to the recognition of zinc as an elementary body. Aristotle, in the fourth century B.C., mentions the preparation of brass under the name of Mossinœcian copper, which he describes as being bright and light-coloured, not produced by the addition of tin, but by its having been melted with a peculiar earth found on the shores of the Black Sea. The early use of brass is clearly proved by the following analysis by Tookey, quoted by Percy, of an undoubtedly genuine Greek coin of Trajan struck in Caria A.D. 110:—

Copper	77·590
Zinc	20·700
Tin	0·386
Iron	0·273
	98·949

This ore, by means of which copper could be coloured yellow, was termed Καδμεία or *cadmia*, by Dioscorides and Pliny. The same word is also used by the latter author to designate the sublimate, consisting of impure oxide of zinc, found in the brassfounders' furnaces. It has already been stated in the Historical Introduction that the older alchemists were acquainted with the means of turning copper a yellow colour. The material by which this change was brought about was

[1] *Jahresb.* 1883, 42. [2] *Amer. Chem. Journ.* 1892, **12**, 219.

termed in the Latin translation of their works *tutia*. Agricola believed that brass was a mixture of copper and earth termed galmei or calamine, and he describes the employment of cadmia in the place of the natural ore as follows: "Sunt qui in cadmiæ fossilis locum cadmiam fornacum substituunt."

The word zinc is first found in the writings of Paracelsus who first pointed out that zinc was a metal. He says in his treatise on minerals: "There is another metal called the *zinken*, which is unknown to the fraternity, and is a metal of a very singular kind." In other places he describes it as a bastard or semi-metal. The word zinc occurs in many subsequent authors, and sometimes it is employed to denote the metal, at other times the ore from which the metal is obtained. Libavius was the first to investigate the properties of zinc more exactly, although he was not aware that the metal was derived from the ore known as calamine. He states that a peculiar kind of tin is found in the East Indies called calaëm. Some of this was brought to Holland and came into his hands. He describes its outward appearance and general properties minutely, and compares them with those of the other metals, laying very particular stress upon the fact that when heated in the air this metal takes fire and burns. The exact nature of zinc and its ores continued doubtful during the seventeenth century. Glauber, it is true, stated that calamine was an ore of zinc, but Lemery so late as 1675 believed that zinc was identical with bismuth, and Boyle often employed the names zinc and bismuth indiscriminately for the same substance, also employing the word spiauter (our English spelter), a name apparently of Eastern origin. In general it was believed that the brass which was obtained from copper and calamine contained the latter substance as such. The view that brass is an alloy was first put forward by Kunkel at the end of the seventeenth century. He says in his *Laboratorium*, "I have already remarked in my annotations that calamine allows its mercurial (metallic) part to pass into the copper and form brass. For thou wilt never believe that as a *sal* it could tinge copper; as a *terra* it cannot enter it, since it would make the copper brittle, and moreover could not tinge it." Stahl afterwards gave it as his opinion that calamine could turn copper into brass by being first converted into zinc.

The preparation of zinc on the large scale appears to have been first carried out in England. According to Bishop Watson, zinc-works were first established at Bristol about the year 1743.

"In about the year 1766 Watson visited Mr. Champion's works near Bristol and saw the process of making zinc, which at that time was kept rigidly secret. Many years afterwards he published an accurate description of this process, which is the same as that hereafter described as the English process" [1] (Percy).

The first Continental zinc works were erected in 1807 at Liège.

Zinc is said to have been found in the native state near Melbourne in Australia, but it occurs chiefly as calamine, smithsonite or zinc-spar, $ZnCO_3$, found near Altenberg, in the neighbourhood of Aix-la-Chapelle, at Wiesloch, in Belgium, Spain, Siberia, and North America, as well as at Alston Moor, Lead Hills, Donegal, and Matlock in Great Britain. It also occurs as siliceous or electric calamine, $Zn_2SiO_4 + H_2O$, found together with zinc spar, and as zinc blende or zinc sulphide, ZnS, occurring with galena, fluor-spar, &c., in England, in the Harz, in Saxony, in Bohemia, in North America, and in other localities.

Other ores of zinc are franklinite $(ZnFe)O + Fe_2O_3$; red zinc ore, or oxide of zinc, which derives its peculiar colour from the presence of red oxide of manganese; hydro-zincite, $ZnCO_3 + 2Zn(OH)_2$; aurichalcite, $2CuCO_3 + 3Zn(OH)_2$; zinc sulphate, $ZnSO_4 + 7H_2O$, and gahnite or zinc-spinelle, $ZnO + Al_2O_3$, &c. Zinc has been found in the ashes of the yellow pansy (*Viola Calaminaris*), growing in Rhenish-Prussia in soil which contains zinc. In former times calamine was the only ore of zinc from which the metal was extracted. At the present time, however, large quantities of zinc silicate, a mineral occurring with the carbonate, are employed for the preparation of zinc, whilst zinc blende is also used. In America the metal is extracted from franklinite and from the red zinc ore.

246 *Smelting of Zinc.*—The first process in the preparation of zinc usually consists in the roasting of the ore in order to drive off the carbonic acid and water which it contains, and, in the case of zinc blende, to convert the sulphide into oxide. In roasting the latter ore great care has to be taken to prevent the formation of zinc sulphate, a salt which requires a very high temperature for its decomposition, and which would be again converted, in the process of reduction which follows, into sulphide, and thus cause a considerable loss. Blende is usually roasted in open furnaces, but an improved form of furnace, in

[1] *Metallurgy*, i. 521.

which the sulphur dioxide evolved is condensed, proposed by Messrs. Hasenclever and Helbig, is now frequently employed.[1]

The reduction of the zinc ores was formerly carried on in England by a process termed distillation *per descensum*. The mixture of ore and coal was heated in crucibles closed at the top but having a pipe leading from the bottom closed by a wooden plug. The latter was quickly carbonised, thus becoming porous and allowing the vapour of the reduced zinc to pass down the tube where it was condensed. This plan necessitated a large consumption of fuel and has therefore been abandoned.

In the *Belgian process*, tube-shaped retorts made of refractory fire-clay are employed. In these the mixture of pounded coal and roasted ore is placed. Each retort (*a*, Fig. 123) is about 1 metre in length, and has an internal diameter of about 0·2 m. To the open end a conical earthenware pipe (*b*), 0·24 m. in length, is luted, and the end of this adapter is fitted into a sheet-iron condenser (*c*), the extremity of which is open and about 2·5 cm. in diameter. Forty-eight or more of these retorts are placed in the furnace, being set in a slanting direction to allow the metal to run out. The surface has the form of an arched recess (Figs. 124 and 125), and four such furnaces are usually built together in brickwork setting. A mixture of 2 parts of ground roasted ore and 1 part of coal-dust is brought into the retorts, each holding about 40 lbs. of the mixture. As soon as the temperature has risen high enough, the reduction begins, and carbon monoxide is evolved and burns from the end of the clay adapter with a blue flame. After a while the flame becomes much more brilliant, showing that the metal is beginning to volatilise; the iron condenser is then placed on to the end of the clay adapter, and the metallic vapours are thus condensed. After about two hours the iron condenser is taken away and the oxide knocked out. A ladle is then held under the mouth of the clay adapter, and the melted zinc which has accumulated in the adapter and in the retort is scraped out. The iron receiver is then again fixed in its place, and after a second couple of hours the operation is repeated. It is completed in about eleven hours. The exhausted charge is then removed from the retort and a fresh one introduced. In this

FIG. 123.

[1] *Zeit. Ver. Deutsch. Ins.* 1872, 505.

way two charges are worked off from each retort in twenty-four hours.

In the *Silesian process*, which is the one now most generally adopted, clay retorts or muffles (Fig. 126) about 1 metre long are arranged side by side in the horizontal bed of a reverberatory furnace (Fig. 127). No less than thirty or forty muffles are thus arranged, and these may contain 1,500 to 2,000

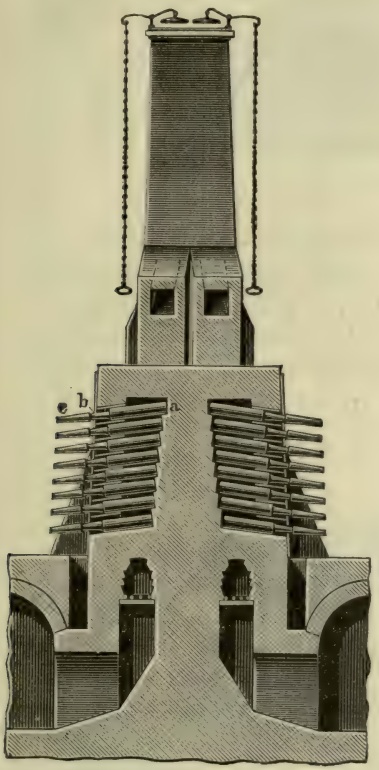


Fig. 124.

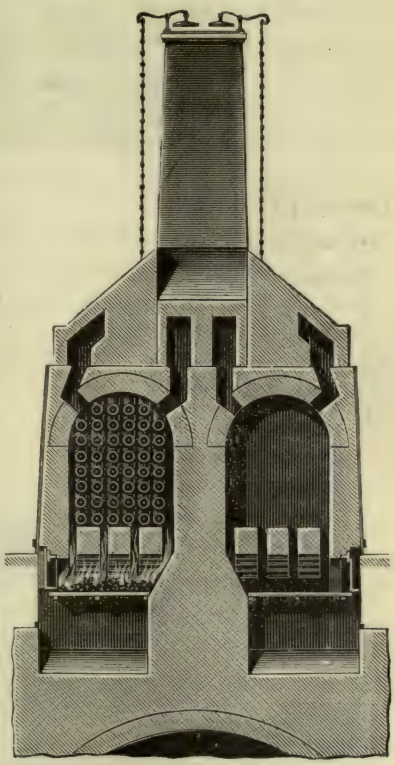


Fig. 125.

kilos. of the mixture of coal and roasted ore. This mixture is introduced through a luted clay door in the muffle or retort. When the temperature has risen sufficiently high, the vapour of the reduced zinc passes out of the retort by a bent clay pipe (A, Fig. 126), and condenses in an iron tube, falling down into an iron tray placed in a closed recess (o, Fig. 127), in the furnace. In this process a considerable quantity of zinc is burnt, producing zinc oxide, known as Silesian zinc-flowers. Siemens'

gas regenerator is now being employed in the zinc-works on the Continent, and in some cases the lower portion of the furnace is filled with Silesian muffles, whilst in the upper part of the furnace the Belgian method is employed.

Commercial zinc is seldom perfectly pure. It almost always contains small quantities of lead, iron, and carbon. Not

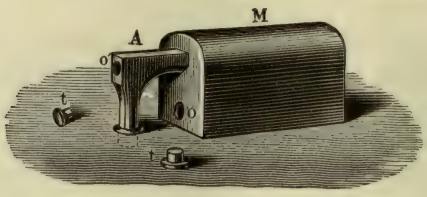


FIG. 126.

infrequently silver, cadmium, and small traces of arsenic, antimony, and other metals are met with. The chemical purity of zinc may be readily ascertained by the fact that, when pure, it is scarcely attacked by dilute sulphuric acid, whereas common impure zinc dissolves readily under the same circumstances (p. 493).

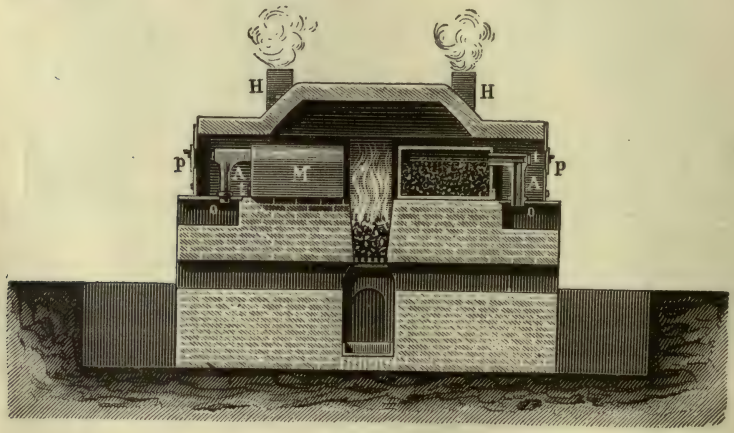


FIG. 127.

247 *Properties.*—Zinc has a bluish-white colour, melts at a temperature of 419° (Heycock and Neville), and boils at 940° (F. Meier and Crafts). The specific gravity of zinc vapour is 2·36, so that its molecular and atomic weights are identical.[1] If zinc

[1] V. Meyer, *Ber.* 1886, **19**, 3295.

be heated to its melting-point, but not to a higher temperature, poured out upon a non-conducting surface, and the molten metal then poured off from the portion which has solidified, the metal is obtained in the crystalline form, consisting of hexagonal prisms and pyramids or rhombohedra. Commercial zinc has a coarsely laminar texture. It is moderately hard, difficult to file, and when bent after fusion it emits a crackling noise, not so loud as that emitted by tin. Zinc exhibits the greatest degree of ductility and malleability at temperatures between 100° and 150°, at which it may be drawn out into wire and rolled into plate.[1] On the other hand, it is so brittle at 205° that it may be powdered in a mortar. The specific gravity of zinc is 6·9. It is largely employed in the form of sheets, for a variety of technical purposes, and also much used in the manufacture of brass, an alloy of the metal with copper. Zinc is also used for desilverising lead, for galvanising iron, for electrical batteries, for the precipitation of gold from its solution in potassium cyanide, and for a great number of other purposes. Metallic zinc in the form of fine dust is obtained in considerable quantity in the manufacture of the metal, mixed with a certain amount of oxide of zinc. This mixture, called *zinc dust*, is a valuable reducing agent, often used for this purpose in organic chemistry, and also on a large scale for the reduction of indigo blue: it is likewise employed as a paint for iron articles. In order to free the powder from oxide of zinc, it is only necessary to allow it to remain for some time in contact with very dilute hydrochloric acid. The residue is first washed with water and then with pure alcohol, after which it is dried and preserved.

Pure zinc is very slowly dissolved by dilute sulphuric acid, whilst the impure substance readily dissolves with evolution of hydrogen. The inactivity of the former is due to the fact that a film of hydrogen forms on the surface of the zinc and prevents the further action of the acid; if however impurities are present these form galvanic couples with the zinc, and as they are electro-negative to zinc the hydrogen is evolved from them, leaving the surface of the zinc continuously exposed to the action of the acid.[2] If a few drops of copper sulphate or platinum chloride solution be added to the acid in which the pure zinc is placed, hydrogen is rapidly evolved, owing to the

[1] Hobson and Sylvestra, *Gilbert's Ann.* **24**, 104.
[2] Weeren, *Ber.* 1891, **24**, 1785.

deposition of copper or platinum on the zinc, which acts in the manner above described.

Zinc also dissolves in hydrochloric acid with evolution of hydrogen and formation of the chloride; with nitric acid, solution also takes place with evolution of nitric oxide, nitrous oxide or ammonia according to the conditions of the experiment, the last named uniting with the excess of nitric acid to form ammonium nitrate. Zinc also dissolves in solutions of the alkalis, with evolution of hydrogen, the zinc oxide first formed dissolving in the excess of alkali forming an unstable salt (p. 496).

Alloys of Zinc.

248 The most important alloys of zinc are those which it forms with copper, which, as already stated, were known long before metallic zinc had itself been isolated.

The following table gives the composition of a variety of copper-zinc alloys:—

	Gold-like alloy used by Watch-makers.	Aich's metal.	Brass from			Tombac		Roman coin of the reign of Titus.
			Ocker.	Stöll-berg.	Eng-land.	English.	Viennese.	
Copper...	58·86	60·20	62·24	65·80	70·30	86·38	97·8	96·06
Zinc.....	40·22	38·10	37·27	33·80	29·30	13·61	2·2	2·71
Tin	—	—	0·12	0·25	0·17	—	—	—
Lead ...	1·90	—	0·59	0·28	0·28	—	—	—
Iron.....	—	1·60	0·12	—	—	—	—	0·85
	100·98	99·90	100·44	100·13	100·05	99·99	100·0	99·62

Brass, which has long been known, was up to the year 1780 always made by strongly heating copper together with calamine and charcoal or coal. The coal reduces the calamine to the metallic condition, and the zinc, instead of passing off as vapour, combines with the copper, and forms brass. At the present day, however, brass is prepared by adding the requisite quantity of metallic zinc to molten copper. The composition of brass varies considerably; common brass, sometimes termed English brass, contains about two parts of copper to one of zinc. When more copper is added the colour becomes reddish. That containing

about 80 per cent. of copper is termed German or Dutch brass or tombac. On the other hand, an additional proportion of zinc yields a light yellow metal known as Muntz metal, an alloy which was first prepared by Muntz, in the year 1832, and has since been very largely used for the sheathing of ships. Another such alloy, named Aich's metal from its inventor, is malleable when hot.

Brass and the other copper-zinc alloys are all harder than copper; they are malleable and can be hammered and rolled into thin plates and drawn out to fine wire; they can also be readily worked in the lathe. These properties, as well as their beautiful colour, bright lustre, and cheapness, render them most useful in the arts and manufactures.

COMPOUNDS OF ZINC.

Zinc and Oxygen.

249 *Zinc Oxide*, ZnO.—This compound occurs as the mineral zincite or red zinc ore, which consists of a mixture of zinc oxide with 0·7 to 12 per cent. of red oxide of manganese. It occurs, especially in New Jersey, in red or orange-yellow hexagonal crystals or in a granular mass. Zinc oxide is also occasionally found in the crystalline state in brass-melting furnaces, as well as in the zinc furnaces. It has already been mentioned that the finely divided oxide was known to the ancients as tutia, pompholyx or flowers of zinc, and Dioscorides states that if too much cadmia be employed in the manufacture of brass, pompholyx is formed like tufts of wool,[1] whence the name *Lana philosophica* was given to this substance by the alchemists. The similarity between the oxide of zinc obtained by combustion and flakes of snow led the alchemists to term it *nix alba;* this was translated into German as "weisses Nichts," and retranslated into Latin as "nihilum album."

Zinc oxide is known in commerce as zinc-white, and is prepared on the large scale and used as a paint. It is obtained by the distillation of zinc in earthenware retorts, the burning vapours of the zinc being brought into chambers through which a current of air is passed and the oxide allowed to deposit in a

[1] πομφόλυξ ἐρίων τολύπαις ἀφομοιοῦται.

second chamber. The preparation of zinc-white directly from the ore has lately been carried on at Liège.[1]

The combustion of zinc can be shown by holding thin zinc turnings in the flame of a lamp, or better still, by placing zinc in a white-hot crucible, and exposing the surface to the air or stirring it with an iron rod, when the metal burns with a bright white flame.

Zinc oxide is prepared for pharmaceutical purposes by precipitating a solution of zinc sulphate with sodium carbonate and igniting the basic carbonate thus thrown down. As the commercial zinc sulphate frequently contains Epsom salts (magnesium sulphate) as an impurity, it is best, in order to obtain the pure compound, to dissolve zinc in dilute sulphuric acid, and then either to treat the solution with sulphuretted hydrogen, or to allow the solution to remain for some time in contact with metallic zinc, in order to precipitate the cadmium, copper, arsenic, and other metals. To the filtrate a small quantity of an alkaline solution of sodium hypochlorite is added, in order to throw down the iron, manganese, &c.; the solution is then filtered, and poured in a thin stream into a boiling solution of pure sodium carbonate. The precipitate is washed with boiling water, and, after drying, it is gently ignited in a glass flask or platinum basin.

Zinc oxide has a specific gravity of 5·6; when hot it possesses a lemon-yellow colour, but on cooling it becomes white. When heated in the oxy-hydrogen flame it emits a brilliant white light, and after being thus heated, phosphoresces for some time in the dark. It rapidly volatilises in an electrical furnace, and condenses in long transparent crystals.[2]

It readily dissolves in acids forming the corresponding zinc salts which are colourless, unless the acid be coloured. The normal soluble salts redden litmus solution; they possess a disagreeable metallic taste, and act as poisons and emetics.

Zinc Hydroxide, $Zn(OH)_2$, is obtained as a white powder, when caustic potash, caustic soda, or ammonia is added to a solution of a zinc salt. It is very soluble in an excess of the reagent, zinc oxide acting as an acid-forming oxide towards the strong alkalis, and it is upon this fact that the solution of zinc in alkalis with evolution of hydrogen depends. This reaction takes place especially quickly in presence of metallic iron. If metallic

[1] See Hofmann's *Ber. Entw Chem. Ind.* i. 919.

[2] Moissan, *Compt. Rend.* 1892, **115**, 1034.

zinc be allowed to remain under the surface of a solution of ammonia in contact with iron or copper, zinc hydroxide crystallises from the solution in colourless transparent rhombic prisms (Runge); and if a saturated solution of the hydroxide in caustic potash be allowed to stand, regular octohedra of the compound, $Zn(OH)_2 + H_2O$, are formed (Bödeker).

Zinc and the Halogens.

250 *Zinc Chloride*, $ZnCl_2$.—Impure chloride of zinc was first prepared by Glauber. He describes in his *De furnis novis philosophicis*, published in 1648, an *oleum lapidis calaminaris*, "obtained by dissolving calamine in spirit of salt, and heating the solution, when a thick *oleum* remains as unctuous as olive-oil, and not particularly corrosive, for the spirit of salt has itself been weakened by corroding the calamine and thus lost its acrimony. This oil must be well preserved against the action of the air, otherwise in a few days it attracts so much air to it that it becomes a watery liquid." In 1735 Hellot prepared "butter of zinc," by distilling flowers of zinc with sal-ammoniac; and Pott, in 1741, obtained the same substance by distilling zinc with corrosive sublimate. Gallisch, in 1782, noticed that zinc deliquesced when exposed to the action of dephlogisticated muriatic acid gas (chlorine), and Westrumb, in 1790, observed that when finely divided zinc was dropped into the gas the metal took fire. This historical sketch serves to show the methods by which the anhydrous chloride may be obtained. The same substance is formed when a mixture of anhydrous zinc sulphate and calcium chloride is distilled (Persoz).

Zinc chloride is a white or usually greyish-white mass, soft, like wax, at the ordinary temperature, melting when heated a little above 100° (H. Davy), and subliming at a higher temperature in white needle-shaped crystals. It is very deliquescent, is soluble in alcohol, and boils at 730°, its vapour density being 4·6, corresponding to the normal formula.

A concentrated solution of zinc chloride is best obtained by dissolving zinc, its oxide, or carbonate, in hydrochloric acid, and evaporating the solution to the consistency of a syrup. On the

addition of a little concentrated hydrochloric acid to this syrupy solution, small deliquescent octohedra separate out, having the composition $ZnCl_2 + H_2O$. Zinc chloride is used in surgery as a caustic, and is employed in the laboratory for the purpose of separating the elements of water from many organic substances. It is also employed on a large scale, as is magnesium chloride, for weighting cotton goods. When its solution is evaporated hydrochloric acid is evolved and basic salts are formed; these may also be obtained by boiling the solution of the chloride with zinc oxide and adding water, when precipitates are formed consisting of mixtures of $Zn(OH)Cl$ and $Zn(OH)_2$ in varying proportions. When a solution having a specific gravity of 1·7 is boiled with an excess of oxide, a liquid is formed which has the property of dissolving silk, and this is used for separating silk fibres from those of wool, or of cotton or linen, whilst all of these dissolve in a solution of normal zinc chloride.

Zinc Bromide, $ZnBr_2$, is formed when bromine vapour is passed over the metal heated to redness. It corresponds closely to the chloride in its properties, and on heating sublimes in the form of white needles. It boils at 650°.

Zinc Iodide, ZnI_2.—Zinc and iodine readily unite when they are heated together to form a colourless easily fusible mass which sublimes in four-sided needles An aqueous solution can be easily obtained by warming metallic zinc and iodine together with water. On evaporating the solution, the anhydrous compound separates out in the orm of regular octohedra, which when exposed to the air first absorb water and deliquesce, and then take up oxygen and lose iodine.

Zinc and Sulphur.

251 *Zinc Sulphide*, ZnS, is found as *blende*, which crystallises in the regular system, frequently in hemihedral forms. Its specific gravity varies from 3·5 to 4·2. In the pure state it is transparent, and has a light yellow colour; usually, however, it contains iron and other metals which impart to it a red, brown, or black tint. The same compound is more rarely found as wurtzite in hexagonal crystals. When ammonium sulphide is added to a solution of zinc salt, a white amorphous precipitate

of zinc sulphide is formed; this is soluble in dilute acids, with the exception of acetic acid, with evolution of hydrogen sulphide. When this precipitate is heated in a current of hydrogen, or when zinc oxide is ignited in an atmosphere of sulphuretted hydrogen, zinc sulphide is obtained in crystals which have the form of wurtzite.

Zinc Sulphate, $ZnSO_4$.—This salt, long known under the name of white vitriol, is thus described in the first book of Basil Valentine's *Last Testament*—"Behold the ∇ (water) of Goslar, how a fine white and red vitriol is found there." The name vitriol was applied to all the salts of the common metals possessing a vitreous lustre,[1] and to this day iron sulphate is known as green vitriol, and copper sulphate as blue vitriol.

White vitriol was prepared on the large scale at Goslar, in the Harz, in the sixteenth century. It was obtained by lixiviating the roasted ore, but its composition remained long unknown. Thus, in Lemery's *Cours de Chymie*, published in 1675, we read, "Le vitriol blanc est le plus dépuré de substance metallique." It was, indeed, soon discovered that this salt might be obtained by dissolving calamine in sulphuric acid, but as this ore always contains iron, green vitriol was obtained at the same time. In addition to this, the fact that both green vitriol and blue vitriol when heated become white through loss of water of crystallisation led to still further confusion between these compounds. It was not until 1735 that Neumann suggested that the base of white vitriol consisted of zinc or calamine, and this view was confirmed by Hellot, inasmuch as he obtained the salt by dissolving zinc in dilute sulphuric acid, whilst Brandt showed that brass was obtained from white vitriol by calcining it and heating it with charcoal and copper.

Zinc sulphate occurs not unfrequently in zinc mines, where it is formed by the oxidation of blende. It is, however, usually obtained on the large scale by roasting ores containing sulphide of zinc, afterwards exhausting with water, and evaporating the solution to the crystallising point, when the hydrate $ZnSO_4 + 7H_2O$, isomorphous with Epsom salts, separates out.

[1] "Atramentum candidum potissimum stiriæ figura reperitur Goslariæ, translucidum cristalli instar; nec cæruleum nec viride caret perspicuitate; unde superior ætas atramento sutorio vitrioli nomen imposuit."—AGRICOLA, *De Natura Fossilium*, Lib. III. ed. 1657.

These crystals (Fig. 128) on heating fuse readily in their water of crystallisation. Commercial zinc vitriol is made to assume the shape of a sugar-loaf by stirring this fused mass in wooden troughs with wooden shovels till crystallisation takes place, and subsequently pressing the mass into moulds. Its specific gravity is 1·95; it effloresces slowly in the air, and on heating to 100° loses six molecules of water, the last molecule being only evolved at a moderate red-heat. One hundred parts of water dissolve :—

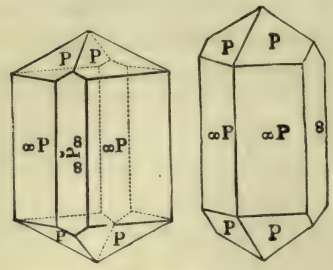


Fig. 128.

At	0°	20°	50°	75°
$ZnSO_4$	41·3	53·0	66·9	80·4.

The anhydrous salt forms a friable mass having a specific gravity of 3·4. When heated more strongly, sulphur dioxide and oxygen are evolved, and a basic salt remains behind, which is also formed when zinc sulphate and zinc oxide are boiled together. On cooling the hot saturated solution, glistening scales separate out having the formula :—

$$SO_2\begin{cases}O—Zn—O—Zn\\ O—Zn—O—Zn\end{cases}O + 2H_2O.$$

At a white heat all the zinc sulphates are completely decomposed, leaving a residue of zinc oxide. When a solution of white vitriol is evaporated above 50° the hydrate $ZnSO_4 + 6H_2O$ isomorphous with the corresponding magnesium salt separates out. Besides these, several other hydrated and basic zinc sulphates are known, and also the characteristic double salts with the alkali sulphates, having the general formula $ZnSO_4,M'_2SO_4 + 6H_2O$.

Zinc sulphate is employed in medicine and in dyeing.

Zinc and Nitrogen and Phosphorus.

252 *Zinc Nitride*, Zn_3N_2, is formed when zincamide is heated to dull redness:

$$3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3.$$

It is a green powder which is decomposed by water with such energy that the mass when moistened becomes incandescent:

$$Zn_3N_2 + 3H_2O = 3ZnO + 2NH_3.$$

Zincamide or *Zinc Diamine*, $Zn(NH_2)_2$, is formed by the action of dry ammonia on zinc ethyl:

$$Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6.$$

It is a white amorphous powder and is decomposed by water with evolution of heat as follows:

$$Zn(NH_2)_2 + 2H_2O = Zn(OH)_2 + 2NH_3.$$

Zinc Nitrate, $Zn(NO_3)_2 + 6H_2O$.—This salt crystallises from a very concentrated solution of zinc in nitric acid, in striated colourless pointed four-sided prisms. These are very deliquescent, and are soluble in alcohol. When heated for some time to 100°, the salt loses water and nitric acid and a basic nitrate remains, which is also formed by boiling the solution with zinc oxide.

Zinc Phosphide, Zn_3P_2, is obtained as a grey mass by heating finely divided zinc in the vapour of phosphorus (Schrötter). When zinc is heated in a current of hydrogen until it begins to melt, and then phosphorus vapour passed over it, together with hydrogen, a fused mass, having a bright metallic bismuth-like lustre is obtained. Zinc phosphide is employed in medicine.

Zinc and Carbon.

253 *Carbonates of Zinc.—Normal Zinc Carbonate*, $ZnCO_3$, occurs as zinc-spar or calamine, crystallising in rhombohedra, having a specific gravity of 4·42. Zinc-spar is found sometimes in the pure state, but in general, more or less of the zinc is found to be replaced by magnesium, cadmium, iron, and other isomorphous metals. When a solution of zinc vitriol is precipitated by an excess of hydrogen potassium carbonate, a white precipitate of the hydrated normal carbonate is obtained. If, on the other hand, normal sodium carbonate be employed, hydrated basic zinc carbonates possessing a variable composition are thrown down which become more basic the higher the tem-

perature at which they are precipitated, and as the quantity of water is increased.

Cyanide of Zinc, $Zn(CN)_2$, is a snow-white powder used in medicine, and prepared by precipitating zinc acetate with aqueous hydrocyanic acid. It is insoluble in water and in alcohol, but dissolves in solutions of the cyanides of ammonium and potassium.

Ammoniacal Derivatives of Zinc.

254 These compounds closely resemble the corresponding derivatives of the divalent copper salts (p. 340). *Zincammonium chloride*, $ZnCl_2,4NH_3 + H_2O$, is obtained by adding ammonia to a solution of zinc chloride until the precipitate first formed redissolves, and on the evaporation of the solution crystallises out in nacreous plates. When heated to 149° it is converted into $ZnCl_2,2NH_3$, which crystallises in rhombic prisms, and on further heating loses ammonia, forming the compound $ZnCl_2,NH_3$; the latter is an amber-coloured mass which distils at a red-heat without decomposition.[1]

Zinc sulphate also yields crystalline ammonia derivatives, having the composition:

$$ZnSO_4,2NH_3 + H_2O,\ ZnSO_4,4NH_3 + 4H_2O.$$

The anhydrous sulphate also combines directly with ammonia forming the compound $ZnSO_4,5NH_3$, which is a white powder and is decomposed by water with separation of zinc hydroxide.

Detection and Estimation of Zinc.

255 The salts of zinc do not as a rule impart any tint to the non-luminous gas-flame, but a few of the salts formed from volatile acids, such as the nitrate, produce a green coloration. The spark-spectrum of zinc is, however, characteristic, and can be well shown by volatilising a small piece of the metal in the lower carbon pole of the electric lamp. Amongst the more prominent zinc lines are 6364 and 6103 in the red, and 4928, 4925, 4912 in the blue.

[1] Kane, *Ann. Chim. Phys.* 1839, **72**, 290.

The most characteristic compound of zinc is the white sulphide insoluble in water, in acetic acid, and in the alkalis. In the ordinary course of qualitative analysis zinc is thrown down together with the other metals precipitated by ammonium sulphide, such as cobalt, nickel, iron, manganese, chromium, and aluminium; the first four are precipitated as sulphides, the last two as hydroxides. The well-washed precipitate is treated with dilute hydrochloric acid, which leaves nickel and cobalt sulphides undissolved; the filtrate is heated with a little potassium chlorate to destroy sulphuretted hydrogen, and oxidise the iron to the ferric state, and ammonia added, which precipitates the iron, chromium, and aluminium as hydroxides. The filtrate is acidified, mixed with an excess of sodium acetate, and sulphuretted hydrogen passed through the solution; zinc is thus precipitated as the sulphide, manganese remaining in solution. When a zinc compound is ignited on charcoal before the blowpipe and the heated mass moistened with a solution of nitrate of cobalt and again ignited, a beautiful green mass, known as Rinmann's green, is obtained. Zinc compounds heated in the blowpipe flame on charcoal with carbonate of sodium yield an incrustation of zinc oxide, which when hot is yellow, but on cooling becomes white.

Small traces of zinc can be readily and accurately detected by *Bunsen's method of flame-reactions.* This depends upon the fact that the more volatile metals, such as zinc, mercury, and arsenic, are reduced from their compounds when these are heated on a thread of asbestos held in the upper reducing-flame of the Bunsen burner. If a small porcelain basin, filled with cold water, be held just above the substance to be examined, the volatilised metal condenses on the outside of the cold basin as a metallic film, and in a few seconds the reaction is complete. A square centimeter of filter-paper is moistened with nitric acid, and this rubbed over the surface of the basin so as to dissolve the metallic film; the paper is then rolled up, placed in a coil of thin platinum wire, and burned in the upper oxidising-flame at as low a temperature as possible, when the colour of the ash is seen to be yellow when hot, but white on cooling. The ash is next moistened with a drop of a dilute cobalt solution, and heated in the flame, when the mass attains a green colour.

For the quantitative determination of zinc, the solution is precipitated with a boiling solution of sodium carbonate, the basic

carbonate washed and dried and converted by ignition into zinc oxide, which is then weighed.

Atomic Weight of Zinc.—This was determined by Marignac[1] from the quantity of zinc and chlorine contained in potassium zinc chloride, K_2ZnCl_4, his results giving an average value of 64·84 (O = 15·88). Baubigny[2] by analysis of the sulphate obtained the number 64·92, and Morse and Burton[3] from the amount of zinc oxide yielded by pure zinc the number 64·78. From the amount of hydrogen obtained by dissolving a known weight of zinc in sulphuric acid, Reynolds and Ramsay[4] obtained the number 65·48, assuming that the weight of a litre of hydrogen was 0·0896 gram. If the later figure of 0·089894 be taken instead of 0·0896 their determinations give the atomic weight 65·26. Gladstone and Hibbert[5] found the ratio of the equivalents of zinc and silver as determined by comparing the quantity of zinc dissolved and silver precipitated by the same current to be 3·298, from which taking silver as 107·13 and oxygen as 15·88, the atomic weight of zinc is found to be 64·97.

Reynolds and Ramsay's number is probably too high, and the true number may be taken as 64·9.

CADMIUM, Cd = 111·3.

256 This metal was discovered in the year 1817 by Stromeyer. He observed that a sample of zinc carbonate obtained from the zinc-works at Salzgitter yielded an oxide which, although it did not contain any iron, possessed a yellow colour, and he found that this was due to the presence of the oxide of a new metal, which he soon afterwards detected in other samples of the oxide of zinc, as well as in metallic zinc itself. Whilst Stromeyer was engaged on these experiments, Hermann, in Schönebeck, also discovered the new metal in a sample of zinc oxide which was employed for pharmaceutical purposes, and which had been confiscated in Magdeburg, inasmuch as the acid solution yielded a yellow precipitate with sulphuretted hydrogen, which was supposed to be caused by the presence of arsenic. Hermann

[1] *Jahresb.* 1883, 42.
[2] *Compt. Rend.* 1883, **97**, 908.
[3] *Amer. Chem. Journ.* 1888, **10**, 311.
[4] *Journ. Chem. Soc.* 1887, i. 854.
[5] *Journ. Chem. Soc.* 1889, i. 443.

showed that this supposition was not correct, and ascertained that a new metal was present. Soon afterwards Meissner and Karsten also observed the existence of the same substance. In 1818 Stromeyer published a complete investigation of the metal, giving to it the name which it now bears, from *cadmia fornacum*, because the metal was chiefly found in the zinc flowers of the zinc furnaces.

Cadmium not only occurs mixed with zinc ores, but likewise as sulphide in the mineral greenockite, a somewhat rare substance found at Greenock, Bishopstown, and Kilpatrick in Scotland, as well as in Bohemia and Pennsylvania. The quantity of cadmium contained in the various samples of calamine and blende varies considerably. The fibrous blende found at Przibram in Bohemia contains 2 to 3 per cent., whilst the calamine of Wiesloch contains 1·6 per cent., and that of Eaton in North America 3 per cent. of cadmium.

In the process of zinc-smelting the more volatile vapour of cadmium comes off with the first portions of the zinc, and these vapours burn in the air with formation of the oxides of cadmium and zinc. The powder thus deposited is then mixed with coal and the mixture heated in iron tubes, when the cadmium distils over first. In order to purify it the metal is redistilled, and the second product dissolved in hydrochloric acid, from which solution the cadmium is precipitated by metallic zinc.

Cadmium possesses a tin-white colour and a fibrous fracture, and takes a high polish. It can be easily crystallised in regular octohedra by sublimation in a current of hydrogen (Kämmerer). It is somewhat harder than tin, but may be cut with a knife. It can be easily rolled out to foil and drawn into wire. When bent, it emits a crackling sound, as tin does when similarly treated. The specific gravity of the cast metal is 8·546, but after hammering it attains a specific gravity of 8·667 (Schröder). It melts at 320° and boils at 763°—772° (Carnelley and Williams). Its vapour has a dark yellow colour and a disagreeable smell, producing headache when inhaled. The density of cadmium vapour is 3·94,[1] and the molecule of cadmium in the gaseous state is therefore monatomic.

Cadmium is employed in the preparation of certain alloys of low melting-point, such as Wood's metal, which consists of eight parts of lead, fifteen of bismuth, four of tin, and three of cad-

[1] Deville and Troost, *Compt. Rend.* 1859, **49**, 239.

mium, and melts at 60°. An amalgam of cadmium was formerly used as a stopping for teeth, but is no longer employed, as it turns the dentine yellow.

CADMIUM COMPOUNDS.

Cadmium and Oxygen.

257 *Cadmic Oxide*, CdO.—This substance forms the brown blaze of the zinc smelters. The metal cadmium burns with a bright flame when heated in the air, forming a brown oxide, which may also be obtained by passing a mixture of steam and cadmium vapour through a red-hot tube. When the metal is heated to whiteness in a current of oxygen, the oxide sublimes in dark red probably cubic, crystals, and may be obtained in the form of a dark blue-black powder, consisting of microscopic octohedra, by igniting the nitrate. Cadmic oxide possesses a specific gravity of 6·5; it does not melt at a white-heat, but is easily reduced at a moderate red-heat on charcoal before the blowpipe; the metal, however, volatilises and burns, and the oxide is deposited as a brown incrustation on the charcoal.

Cadmic Hydroxide, $Cd(OH)_2$, is obtained as a white precipitate by the addition of a soluble salt of cadmium to caustic potash. The hydroxide absorbs carbon dioxide from the air, and at 300° it is resolved into the oxide and water. It is soluble in a solution of ammonia.

This oxide and hydroxide correspond to the only series of cadmium salts definitely known, which are for the most part colourless salts closely resembling those of zinc. The soluble ones have a disagreeable metallic taste and act as emetics. A series of cadmous salts appears, however, to exist, as the cadmic halogen compounds when heated with cadmium yield salts having strongly reducing properties. These have not been obtained pure, the products appearing to consist of mixtures of cadmous and cadmic salts. If the product of the reaction of cadmium on cadmic chloride be treated with water, lustrous transparent crystals first separate out, which soon fall to a white amorphous powder of *cadmous hydroxide*, CdOH The latter on gently heating yields *cadmous oxide*, Cd_2O, as a yellow microcrystalline powder, which on further

heating decomposes into a mixture of cadmium and cadmic oxide, the colour changing to green.[1]

Cadmic Salts.

258 *Cadmium Chloride*, $CdCl_2$.—This salt is obtained by evaporating a solution of the metal or oxide in hydrochloric acid. The hydrated chloride, $CdCl_2 + 2H_2O$, is deposited in the form of rectangular prisms which readily effloresce on exposure to the air, and on heating lose water and melt at a temperature below a red-heat. The transparent pearly mass of the anhydrous chloride sublimes at a higher temperature in transparent micaceous laminæ. Its specific gravity is 3·256. One hundred parts of water dissolve (Kremers):—

At	20°	40°	60°	80°	100°
$CdCl_2$	140·8	138·9	138·9	142·9	142·9

Cadmium Iodide, CdI_2, is obtained by dissolving the metal in hydriodic acid, or by digesting it with iodine and water. It crystallises in large transparent six-sided tables, which do not undergo alteration on exposure to the air. It melts easily, solidifying again to a crystalline mass, but gives off iodine when heated to a higher temperature. It dissolves readily in water and alcohol. Its specific gravity is 4·576. One hundred parts of water dissolve:—

At	20°	60°	100°
CdI_2	92·6	107·5	133·3.

Iodide of cadmium is used in photography, it being one of the few iodides soluble in alcohol.

Cadmium Sulphide, CdS.—Cadmium sulphide occurs in yellow hexagonal glittering crystals as greenockite. It is obtained as a fine yellow precipitate when a cadmium salt is precipitated with sulphuretted hydrogen, this precipitate being employed as a pigment. It melts at a white-heat, and forms on cooling a lemon-yellow micaceous mass, having a specific gravity of 4·86. It is soluble in strong hydrochloric and nitric acids, and in boiling dilute sulphuric acid.

Cadmium Sulphate, $CdSO_4$.—A concentrated solution of sulphate of cadmium when allowed to evaporate spontaneously

[1] Morse and Jones, *Amer. Chem. Journ.* 1890, **12**, 488.

deposits large monosymmetric hydrated crystals, having the composition $3CdSO_4 + 8H_2O$. A boiling saturated solution of the normal salt to which strong sulphuric acid has been added deposits indistinct crystals of $CdSO_4 + H_2O$. The normal salt when heated yields a basic compound, $SO_2 \begin{cases} OCd(OH), \\ OCd(OH), \end{cases}$ difficultly soluble in water, and crystallising in pearly scales. One hundred parts of water at 23° dissolve fifty-nine parts of the anhydrous normal salt, and at the boiling-point a somewhat larger quantity. Crystallised cadmium sulphate is used in diseases of the eye.

Cadmium Nitrate, $Cd(NO_3)_2 + 4H_2O$, crystallises in fibrous needles, which deliquesce in the air, and are soluble in alcohol.

Cadmium Carbonates.—The normal salt is not known. The white precipitate obtained by addition of an alkali carbonate to a soluble cadmium salt possesses a varying composition, according to the temperature at which the precipitation takes place and the amount of precipitant employed. With an excess of potassium carbonate in the cold the precipitate possesses nearly the composition of the normal salt.

Detection and Estimation of Cadmium.

259 Cadmium salts do not impart to the non-luminous gas-flame any tint. The cadmium spectrum is well seen when the metal is volatilised in the electric arc; the most prominent lines being 6438 in the red, 5378 and 5338 in the green, and 5085, 4800, and 4677 in the blue.

The yellow sulphide of cadmium is the most characteristic compound of the metal. This is insoluble in dilute acids in the cold, and hence may be easily distinguished from zinc as well as from the other metals already described. Cadmium sulphide can easily be distinguished from other yellow sulphides, such as those of tin, antimony, and arsenic by its insolubility in ammonium sulphide and in the caustic alkalis. The method of separating cadmium from the other metals precipitated by sulphuretted hydrogen will be discussed under these several metals. It may suffice here to remark that cadmium hydroxide, like the corresponding copper compound, is soluble in ammonia, and that these two metals are frequently obtained together in the process of analysis. In order to separate these, two methods

may be employed. In the first place potassium cyanide may be added to the blue ammoniacal solution until this becomes colourless, and then sulphuretted hydrogen led through the solution, when the cadmium sulphide is completely precipitated. Or, in the second place, the metals may be both precipitated as sulphides, and the washed precipitate boiled with a mixture of five parts of water and one part of concentrated sulphuric acid when the cadmium sulphide is dissolved out.

The quantitative determination of cadmium is usually made by precipitating the carbonate from the boiling solution with sodium carbonate; this is then dried and converted by ignition into the oxide which is weighed. Cadmium may also be determined as the sulphide which is dried at 100° and then weighed.

Atomic Weight of Cadmium.—The atomic weight of cadmium was found by Huntington[1] from the analysis of the bromide to be 111·4 (O = 15·88), and by Morse and Jones[2] by the conversion of pure cadmium into cadmic oxide to be 111·23; Lorimer and Smith[3] by the electrolytic reduction of cadmic oxide in potassium cyanide solution obtained the number 111·21.

MERCURY (Hydrargyrum), Hg. = 198·9.

260 We do not find this metal mentioned either in the books of Moses or in the writings of the older Greek authors. Theophrastus (B.C. 300) speaks of liquid silver or *quicksilver* (χυτός ἄργυρος), and says that it is obtained by rubbing cinnabar with vinegar in a copper vessel. Dioscorides in the first century mentions this body as ὑδράργυρος (from ὕδωρ water and ἄργυρος silver), and states that it is obtained by subliming cinnabar and charcoal in an iron pot, upon which a cover is luted. Pliny, who named the material thus obtained *hydrargyrum*, in contradistinction to the native mercury to which he gave the name of *argentum vivum*, was acquainted with the fact that all solid bodies with the exception of gold, swam on the surface of the liquid metal. Isidorus, in the beginning of the seventh century, was also acquainted with the properties of mercury, as is seen

[1] *Ber.* 1882, **15**, 80. [2] *Amer. Chem. Journ.* 1892, **14**, 261.
[3] *Zeit. anorg. Chem.* 1891, **1**, 364.

from the following extract: "Argentum vivum servatur melius in vitreis vasis, nam caeteras materias perforat."

Mercury was known to the older alchemists, who were much interested in the examination of its properties, inasmuch as they believed this body, or some substance closely resembling it, to be one of the component parts of all metals. They were acquainted with the method of purifying it by distillation, and they knew how to prepare many of its compounds. During the epoch of iatro-chemistry, the properties of the mercury compounds were more minutely examined, especially with regard to their medicinal properties. Agricola regarded mercury as a metal, but Libavius placed it amongst those "quæ metallis sunt affinia," thus connecting it with bismuth, arsenic, galena, cinnabar, and other bodies. Even at a later date many chemists held similar views; thus Brandt in 1735 spoke of it as a semi-metal, and indeed it was not reckoned as a true metal until Braune, of St. Petersburg, in the winter of the year 1759, found that it solidified when exposed to a freezing mixture made of snow and nitric acid.

Mercury occurs in the native state, though in small quantity as compared with its other ores. It is found in globules disseminated through the native sulphide in the Palatinate, in Carniola, Hungary, Peru, California, and other countries. It also occurs as silver- and gold-amalgam, as the iodide and chloride, and it is found occasionally in certain fahl-ores. The most important ore of mercury is the sulphide or cinnabar. The most celebrated mercury mines are those of Idria, in Carniola; Almaden, in Spain; in California, especially in the Pioneer Mine in Napa Valley; and at Wolfsstein and Landsberg, in the Bavarian Palatinate. Cinnabar is likewise imported into this country from China and Japan.

261 For the purpose of extracting mercury from rich ores, a furnace is employed in the Idrian works, shown in Figs. 129 and 130. This consists of a fire (*A*), over which three concentric arches (*aa*, *bb*, *cc*) are built; these are perforated to allow the flame and heated air to pass through, the ore being placed on the top of the arches. The action of the air and flame on the ore is to volatilise the mercury and oxidise the sulphur to sulphur dioxide. The vapour of the mercury and the gases find their way through the chambers (C, C, C,) in which the mercury is deposited, and the condensed metal flows by the passages (*x y z*) into underground reservoirs. The last chambers (*D* and *E*) serve for the

condensation of the aqueous vapour and finely-divided mercury, and this impure dust is collected and again subjected to the process of distillation. In order to collect every trace of mercury a current of water meets the ascending gases in the tower or chamber (*D*).

The mercury thus obtained is filtered through linen, and exported generally in iron bottles, but sometimes in leather bags. The largest furnace in Idria, erected in the year 1794, is about 10 m. high and 60 m. long; this is charged with from 50 to 60 tons of ore, and yields from 4 to 4·5 tons of mercury; 40 workmen can fill the furnace in 3 hours, and each distillation

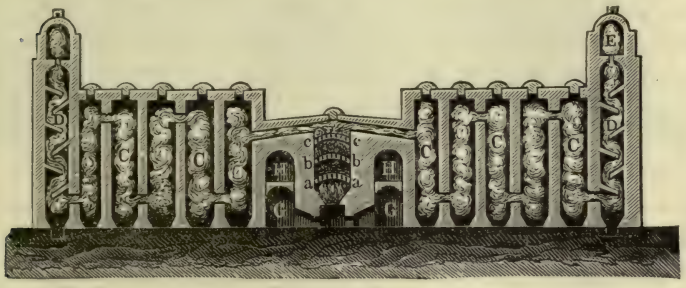


Fig. 129.

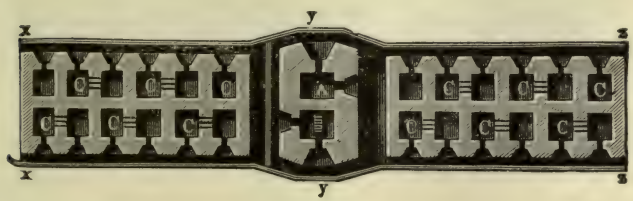


Fig. 130.

lasts 12 hours; but the furnace must be allowed to cool for from 4 to 5 days before it can be charged a second time.

For the treatment of ores poor in mercury, a furnace known as the Alberti furnace is employed in the Idrian works. About a ton of ore is introduced into the hearth and spread over a third of the area of the hearth at the back. After it has been exposed for several hours to the flames from the furnace it is raked forward to the centre of the furnace, a fresh charge being introduced at the back, and after a similar interval the first charge is raked into the front of the hearth, the second brought

forward to the middle, and a third charge introduced at the back. In the succeeding interval the mercury is completely removed from the front charge, and the residue is then raked through an opening in the front of the furnace into a chamber beneath, the other charges being brought forward as before and a fresh charge introduced at the back. The products of combustion together with the mercury vapours pass into a large chamber, and thence by means of a series of inclined cast-iron tubes and intermediate condensing chambers into the chimney stack. The condensation in this furnace is almost complete, 95 per cent. of the mercury separating out in the lower iron tubes, from which it is run off as it is formed. Considerable quantities of carbonaceous matter also separate out in the flues, together with some metallic mercury and cinnabar, which after a time block the tubes, and necessitate the stoppage of the furnace for cleaning.

A similar process to that employed near Idria is adopted at Almaden, except that the vapours instead of passing through condensing chambers traverse a series of tubes made of earthenware, called *aludels*. These are open at both ends, and fit into one another in a similar way to the condensers employed in the manufacture of iodine. The aludels are arranged one behind the other, first in a descending, and then in an ascending position on arches of masonry (Figs. 131 and 132); the greater part of the mercury condenses in and runs from the aludels, *a* (Fig. 131) into the channel *b*, and then into the cisterns (*r r*). The shape and arrangement of the aludels is shown in Fig. 133. A small quantity of mercury vapour passes on into chamber (C), where it condenses, coming in contact with water contained in the vessel (*i*).

262 The mercury of commerce usually contains a certain proportion of dissolved foreign metals, and these impurities give rise to the "tail" seen when the metal is allowed to run over a slightly inclined surface. Impure mercury, when shaken with air, yields a black powder, caused by the oxidation of the metallic impurities, and this film of oxide incloses a small globule of the liquid metal. The surest mode of freeing mercury from these foreign metals is to distil it, the surface being covered with iron filings to prevent the spitting of the metal, which, however, cannot be completely avoided. It is a curious fact that when small quantities of lead or zinc are present in the mercury the rate of distillation is much diminished. The distillation

is frequently carried out in vacuo, numerous forms of apparatus for this purpose having being proposed. Mercury may be more easily purified by treating it with dilute nitric acid, the impurities being the first to dissolve. In order to bring the

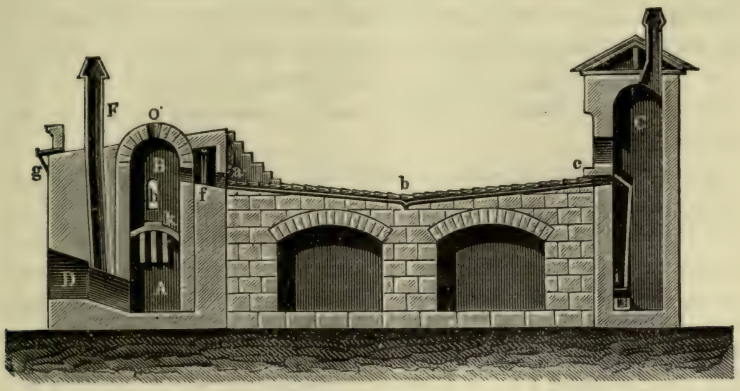


Fig. 131.

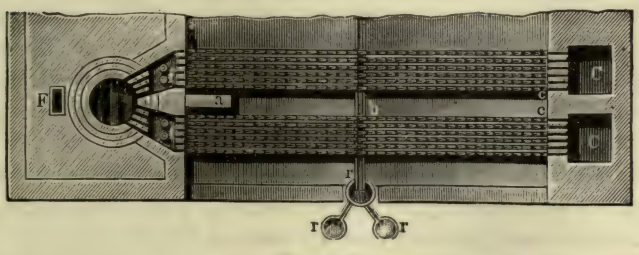


Fig. 132.

mercury into contact with the acid it is either exposed in thin layers in a shallow vessel, or is frequently shaken up with the acid. The following improved method for the purification of

Fig. 133.

mercury by means of nitric acid has been suggested by L. Meyer:[1] The metal is allowed to flow in a very thin stream from a small opening in a glass funnel into a wide glass tube 1·25 m. high and 5 cm. in diameter, which contains a

[1] *Zeit. anal. Chem.* 1863, **2**, 241.

mixture of water and 100 cc. of nitric acid. A narrow tube is fastened to the bottom of this, from which the pure metal flows; it has then only to be washed with water and dried. The above operations may have to be repeated several times, and the metal, if pure, must leave no residue when dissolved in pure nitric acid, evaporated to dryness and ignited. It may also be purified by placing in a long slightly inclined tube and drawing air through the latter for several days; the impurities are thereby oxidised, and separate as a scum on the surface.

Pure mercury possesses a silver-white colour. It is liquid at ordinary temperatures, and the globules retain a perfectly spherical shape. The freezing-point of mercury was first determined by Hutchins in 1783, at Fort Albany, in Hudson's Bay Territory, according to instructions received from Cavendish; its melting-point is $-38°{\cdot}85$. In the act of freezing, mercury contracts considerably, giving rise to a solid tin-white ductile malleable mass, crystallising in octohedra, capable of being cut with a knife, and having a specific gravity of 14·1932.[1]

The liquid metal is transparent when in very thin films and transmits violet-blue light: (Melsens). When a powerful stream of water is poured from a height of a decimeter on a mass of from 15 to 20 kilos. of mercury, bubbles of the metal, of about 1 cm. in diameter, are seen swimming on the surface of the water. These consist of very thin films of mercury, through which blue light is transmitted; they soon burst, and leave behind a very small solid globule of the metal.

The specific gravity of mercury at 0°, compared with water at 4°, is 13·595 (Kopp), whilst the specific gravity of mercury weighed in a vacuum at 4° is 13·594. (Balfour Stewart.) The boiling-point of mercury, according to Regnault's observations, is $357°{\cdot}25$, the metal giving rise to a colourless vapour, which has a specific gravity, according to the experiments of Dumas, of 6·976, or, according to those of Bineau, of 6·7; the molecule of mercury in the gaseous condition is therefore, like those of zinc and cadmium—monatomic. In spite of its high boiling-point, mercury volatilises perceptibly at the ordinary temperature, both in a vacuum and in air, as proved by the "silvering" of gold-leaf kept for two months in a vessel over mercury (Faraday); and Merget has shown that even at $-44°$, when mercury is solid, it still possesses a distinct vapour-tension.

[1] Mallet, *Proc. Roy. Soc.* 1877, p. 77.

The tension of the vapour of mercury has been determined by Regnault,[1] and is given in the following table —

Temperature.	Tension in mm.	Temperature.	Tension in mm.	Temperature.	Tension in mm.
0°	0·0200	180°	11·00	360°	767·74
10	0·0268	190	14·84	370	954·65
20	0·0372	200	19·90	380	1136·65
30	0·0530	210	26·35	390	1346·71
40	0·0767	220	34·70	400	1587·96
50	0·1120	230	45·35	410	1863·73
60	0·1643	240	58·82	420	2177·53
70	0·2440	250	75·75	430	2533·01
80	0·3528	260	96·73	440	2933·99
90	0·5142	270	123·01	450	3384·35
100	0·7455	280	155·17	460	3888·14
110	1·0734	290	194·46	470	4449·45
120	1·5341	300	242·15	480	5072·23
130	2·1752	310	299·69	490	5761·32
140	3·059	320	368·73	500	6520·25
150	4·206	330	450·91	510	7353·44
160	5·900	340	548·35	520	8264·96
170	8·091	350	663·18		

When mercury is contaminated with oxide or its halogen derivatives it adheres to glass, forming a bright mirror. (Shenstone). When shaken with different liquids, or when it is triturated with sugar, sulphur and other bodies, the liquid metal is obtained in a very finely divided state, being converted into a grey powder. This was formerly termed *Aethiops per se.* This act of fine division is termed the "extinction" or "deadening" of mercury. Grey mercurial ointment is formed by rubbing up mercury and fat together, and in the preparation the mercury is in the form of globules having a diameter of 0·002 to 0·004 mm.

Mercury is largely used in the preparation of physical and chemical apparatus, for collecting gases which are soluble in water, for the preparation of mirror plates, for the amalgamation of silver and gold, for the preparation of the mercurial compounds, and in the electrolytic production of caustic soda.

[1] *Compt. Rend.* 1871, **73**, 1356, see also Ramsay and Young, *Journ. Chem. Soc.* 1885, i. 656.

ALLOYS OF MERCURY OR AMALGAMS.

263 The general properties of these alloys have already been given on page p. 72 of this volume.

Potassium Amalgam.—Potassium combines with mercury with evolution of heat but without incandescence, forming a silver-white compound, which is liquid when it contains one part of potassium to about seventy parts of mercury, but when it contains more potassium it becomes solid. If the metals be melted together in the right proportions, or if sodium amalgam containing 3 per cent. of the alkali metal be brought into potashley a crystalline compound $Hg_{12}K$, is formed, which in the last mode of preparation is obtained crystallised in very bright shining cubes or dodecahedra and rhombohedra.[1] When an amalgam, rich in potassium, is heated to 440° a crystalline compound, HgK_2, remains behind, which takes fire spontaneously on exposure to air.[2]

Sodium Amalgam.—Sodium combines violently with mercury evolving light and emitting a hissing noise. One part of sodium to 100 of mercury forms an amalgam having an oily consistency, but with 80 of mercury to 1 of sodium a pasty mass is obtained, and with smaller quantities of mercury a hard and crystalline amalgam is formed. When an amalgam containing 3 per cent. of sodium is allowed to stand under water, long needles having the composition Hg_6Na separate out (Kraut and Popp), and when an amalgam rich in sodium is heated to 440° the crystalline compound $HgNa_3$ remains (De Souza).

The amalgams of the alkali-metals decompose slowly on exposure to moist air and water, and amalgamate iron and platinum. Sodium amalgam is employed in the processes of extracting silver and gold, and also in organic chemistry as a reducing agent.

Ammonium Amalgam.—This compound, discovered at the same time by Berzelius and Pontin,[3] and Seebeck,[4] has already been described (p. 285).

Cadmium Amalgam.—Cadmium easily dissolves in warm mercury, giving rise to a solid compound, Hg_5Cd_2, which has a specific gravity of 12·615. When mercury is saturated with

[1] Kraut and Popp, *Annalen*, 1871, **159**, 188.
[2] De Souza, *Ber.* 1876, **9**, 1050.
[3] *Gilbert's Ann.* **6**, 260.
[4] Gehlen, *Neu. Allg. Jour. Chem.* **5**, 482.

cadmium a silver-white compound, Hg_2Cd, crystallising in octohedra, is formed. This is very brittle, and is heavier than mercury, and was at one time used as a stopping for teeth.

Copper Amalgam.—If copper foil be rubbed with a solution of nitrate of mercury it becomes covered with a bright lustrous coating of the metal, and if a line be drawn with this solution on a piece of brass foil and the foil bent at this place, it can easily be broken, as the mercury very soon penetrates the copper and renders it brittle. Copper amalgam is obtained by rubbing a copper rod with the nitrate solution and then allowing it to remain in contact with mercury under warm water. All the copper amalgams which contain from 25 to 33 per cent. of copper, when heated to 100° become plastic when rubbed in a mortar. After from ten to twelve hours the amalgam loses its plasticity and assumes a granular crystalline structure and is hard enough to engrave upon tin. Its density is the same in the soft and hard states and, therefore, it does not expand in hardening, and thus fills cavities when hard into which it has been pressed in the soft state. This amalgam is used for stopping teeth, but the copper which it contains renders it objectionable on account of its tendency to blacken. It is also used for sealing bottles, glass tubes, &c., when other plastic substances such as cork cannot be used, as well as for taking impressions of engraved metal work.

Silver Amalgam occurs as a mineral at Moschellandsberg, in the Palatinate, and crystallises in the regular system. It is artificially prepared as the silver-tree (*arbor Dianæ*) by pouring mercury into a solution of silver nitrate. The composition of the product thus deposited as well as that of the natural amalgam varies considerably. When silver amalgam is heated to 440° the compound Hg_3Ag remains (De Souza).

COMPOUNDS OF MERCURY

Mercury and Oxygen

264 These elements form two compounds:

Mercurous oxide Hg_2O.
Mercuric oxide HgO.

Mercurous Oxide, Hg_2O.—This compound, also called sub-oxide or gray oxide of mercury, is easily obtained by the

action of caustic alkalis in excess on a mercurous salt. It is a blackish-brown powder, which by the action of light and a moderate temperature, as well as when brought in contact with different saline solutions, is decomposed into the metal and the monoxide. It corresponds to the series of *mercurous* salts, in which the metal is probably monovalent. The neutral salts with colourless acids are colourless or pale yellow, and the halogen derivatives with the exception of the fluoride are insoluble in water; the salts with oxyacids only dissolve in presence of free acid, pure water converting them into soluble acid salts and insoluble basic salts. They have a metallic taste, and are poisonous, although less so than the mercuric salts.

Mercuric Oxide or Mercury Monoxide, HgO; commonly termed *Red Oxide of Mercury*, or *Red Precipitate*.—This compound was known to the Latin Geber, who obtained it by heating mercury in the air for a long time. It was afterwards known by the name of *mercurius præcipitatus per se*. The same compound is formed when a solution of mercury in nitric acid is evaporated, and the residue heated; the compound thus prepared was called by Raymond Lully *mercurius præcipitatus ruber*.

When mercury is exposed in a glass flask with a long neck for several weeks to a temperature somewhat below its boiling point, small red crystals of the oxide appear on the surface, and this product, which has a dark-red colour and is highly crystalline, increases gradually in quantity. Mercuric oxide is prepared on the large scale by heating an intimate mixture of mercury and mercuric nitrate until no further red fumes are given off: in this way it is obtained in the form of bright, brick-red crystalline tablets, which have a specific gravity at 4° of 11·136 (Joule and Playfair).

When a solution of a mercuric salt is precipitated by caustic potash or soda, a yellow precipitate is obtained which has usually been regarded as anhydrous mercuric oxide, but Carnelley and Walker[1] have shown that when dried in the air it is in reality *mercuric hydroxide*, $Hg(OH)_2$, which only loses water very slightly at 100°, but at 175° is completely converted into *yellow mercuric oxide*. When heated to 415—440° it is converted into the red oxide with simultaneous partial decomposition into mercury and oxygen.

Mercuric oxide is a powerful poison, it possesses an unpleasant metallic taste and an alkaline reaction, and is slightly

[1] *Journ. Chem. Soc.* 1888, i. 80.

soluble in water. When heated it first changes to a dark cinnabar-red colour, and afterwards assumes a black tint, but on cooling it resumes its original appearance. At a red-heat it decomposes into its elementary constituents, and on cooling these partially recombine. The metallic mercury which is thus formed does not possess perfect fluidity, but attains its usual mobile character on treatment with dilute nitric acid.

When the oxide is heated with sulphur explosions occur, and it is also decomposed when brought in contact with fused sodium, with evolution of light and heat.

Mercuric oxide is used in medicine, and is valuable for various purposes in chemical analysis.

The mercuric salts correspond to this oxide, and are obtained from it by neutralising with acids or in many cases by the action of an excess of acid on metallic mercury. The normal salts with colourless acids are also colourless, but frequently yield yellow basic salts. They are converted by reducing agents into mercurous salts, these latter being further reduced to metallic mercury in presence of an excess of the reducing agent. The soluble salts have a metallic taste, redden blue litmus, and are extremely poisonous (see p. 535).

Mercurous Salts

265 *Mercurous Fluoride*, HgF or Hg_2F_2, is a yellow crystalline salt which is soluble in water.

Mercurous Chloride, HgCl or Hg_2Cl_2, is commonly known as *calomel*. Calomel occurs as a mineral termed horn-quicksilver, is found at Moschellandsberg, Idria, Almaden and other places, and crystallises in rhombic prisms. The artificial substance has been known for a long time, and it appears to have been used in the sixteenth century as a medicine, known by the name of *Draco mitigatus*, *Manna metallorum*, *Aquila alba*, or *Mercurius dulcis*. It afterwards received the name calomel, which it now bears, from καλομελας, a fine black colour, because it turns black when acted upon by an alkali.

Mercurous chloride is formed by the direct union of its elements, and also by the action of hydrochloric acid or common salt solution on a dilute solution of mercurous nitrate. In order to prevent a basic nitrate being carried down with the insoluble chloride, an excess of hydrochloric acid or salt solution must be

added, and the liquid must be warmed with the precipitate for some time. In this way it is obtained in the form of a yellowish-white impalpable powder.

Calomel is commonly prepared by sublimation. For this purpose an intimate mixture of mercuric chloride (corrosive sublimate) and mercury in the right proportions is heated. Another, and now nearly obsolete process, is to rub up dry mercuric sulphate in a mortar with as much mercury as it already contains, and an equal quantity of common salt, until the globules disappear and a uniform mixture is produced. This is then sublimed, the vapour of calomel being carried into an atmosphere of steam or into a chamber containing air, where it is condensed into a finely-divided form, and thus the labour of powdering it is avoided. The following decomposition occurs:—

$$HgSO_4 + Hg + 2NaCl = 2HgCl + Na_2SO_4.$$

The sublimed powder thus obtained is well washed to free it from any traces of corrosive sublimate which it may contain, and dried ready for use. When dissolved in hot mercurous nitrate solution, and allowed to cool, it separates out in yellowish-white quadratic plates.

Calomel is tasteless and insoluble in water, and has a specific gravity of 6·56. It evaporates at a red heat without fusion, yielding a colourless vapour, whose specific gravity is 8·21 (Deville and Troost); this corresponds to a vapour density of 117·59, whereas the theoretical density corresponding to the formula HgCl is 117·58. It has however been shown by Harris and V. Meyer[1] that the vapour is completely dissociated into mercury and mercuric chloride (see p. 35), and therefore no conclusion can be drawn from the vapour density as to its molecular formula. It has frequently been suggested that as in many respects mercurous chloride strongly resembles cuprous chloride, it has a formula analogous to that of the latter, namely, Hg_2Cl_2, but no definite proof of this has been obtained by any of the usual methods; until such proof is forthcoming it is preferable to employ the simple formula for this and other mercurous salts.

Calomel is largely employed in medicine, the precipitated

[1] *Ber.* 1894, **27**, 1483, 3143; see also Fileti, *Gazzetta*, 1881, 341; *J. pr. Chem.* 1894 (2), **50**, 222; 1895 (2), **51**, 197.

compound being more active in its medicinal properties than that prepared by sublimation, owing to its finer state of division. In certain cases abnormal poisonous effects have been produced by calomel, which have probably been caused by the presence of basic mercurous nitrate.

Mercurous Bromide, HgBr, is obtained as a heavy white precipitate by adding hydrobromic acid or potassium bromide to mercurous nitrate solution. It is obtained in white nacreous quadratic plates by shaking a solution of mercurous nitrate with bromine water or an alcoholic solution of bromine. It sublimes at 340—350° without decomposition,[1] and slowly decomposes in the light.

Mercurous Iodide, HgI, is prepared by rubbing mercury with mercuric iodide or iodine in the requisite proportions, and then forms a greenish coloured powder, which is however not pure. If an excess of iodine be boiled with a solution of mercurous nitrate containing a little nitric acid, mercurous iodide separates on cooling in transparent yellow quadratic plates, which gradually blacken in the light. On heating, the colour changes successively to dark yellow, orange and garnet red, and on cooling the same colours are observed in the reverse order; it commences to sublime at 110—120°, and melts and decomposes at 290°.[2] In the form of powder it is used in medicine.

Mercurous Sulphide does not exist, a mixture of metallic mercury and mercuric sulphide being produced in cases in which its formation might be expected.

Mercurous Sulphate, Hg_2SO_4, is formed by heating concentrated or fuming sulphuric acid with an excess of mercury, or by precipitating mercurous nitrate with sulphuric acid. It is a white crystalline powder which when gently heated melts, and on cooling solidifies to a crystalline mass. It is precipitated almost completely by sulphuric acid from its solution in nitric acid. It is easily soluble in hot sulphuric acid; part of it separates out on cooling, and the remainder is precipitated on the addition of water.

Mercurous Nitrate, $HgNO_3$, is formed by the action of dilute nitric acid in the cold on mercury. Hot nitric acid, on the other hand, especially if an excess of acid be employed, forms mercuric nitrate. Bergman was the first to point out the difference between the two solutions thus obtained, the explanation, according to the then prevalent

[1] Stroman, *Ber.* 1887, **20**, 2822. [2] Stroman, *Ber.* 1887, **20**, 2818.

views, being that the solution of the metal in cold nitric acid contained less phlogiston than that in the hot acid. At a later period the same fact was explained by stating that in the former the mercury was less strongly oxidised than in the latter case.

Mercurous nitrate crystallises in monosymmetric tables or prisms, containing two molecules of water of crystallisation, which it loses on exposure to dry air or over sulphuric acid. The salt dissolves in a small quantity of warm water; on the addition of more water a basic salt is formed. It is easily soluble in dilute nitric acid, and this solution brought on to the skin colours it, first purple and then of a black tint. By the continued action of nitric acid upon an excess of mercury the basic double salt, $3HgNO_3$, HgOH, is formed together with the normal nitrate. This basic salt crystallises in long, thin, rhombic prisms, and if this salt or the normal salt be boiled for some time with mercury, the water being replaced as it evaporates, large, colourless, hard, glistening asymmetric prisms, having the formula $3HgNO_3$, 2HgOH, are deposited when the solution is allowed to cool. By the protracted action of cold water on the different mercurous nitrates a yellowish crystalline salt, having the composition $HgNO_3$, HgOH, is formed; this is decomposed on boiling with water into mercury and mercuric nitrate.

Mercurous Carbonate, Hg_2CO_3, is obtained by precipitating the nitrate with hydrogen potassium carbonate. In order to remove a quantity of basic nitrate which is thrown down at the same time, the potassium carbonate is added in excess, and the solution allowed to stand for some days. Mercurous carbonate is a yellow powder which decomposes at 130° into carbon dioxide, mercury, and mercuric oxide and blackens on exposure to light (Lefort).

Mercuric Salts

266 *Mercuric Fluoride*, $HgF_2 + 2H_2O$, is formed by the action of excess of hydrofluoric acid upon the oxide. It is a white crystalline mass which decomposes at 50°, with formation of the yellow oxyfluoride, HgF(OH), which is also obtained when an excess of mercuric oxide is treated with hydrofluoric acid. On slow evaporation it separates in dark-yellow crystals.

Mercuric Chloride, $HgCl_2$.—This salt is obtained when

mercury is heated in chlorine. It was first obtained by the Latin Geber according to the following receipt: "Sublime *Argentvive* thus: Rc. of it *lib.j.* of *vitriol* rubified, *lib. ij.* of *rock-allum* calcined, *lib. j.* of *common salt*, *lib. semis.* and of *salt-peter* one fourth part. Incorporate all together, and sublime: and gather the *white*, *dense*, and *ponderous*, which shall be found about the *sides* of the *vessel*, and keep it, as we have appointed of other things. But if, in the first *sublimation*, you shall find it turbid, or unclean (which may happen, by reason of your own negligence), again sublime it with the same *feces*, and reserve it for use." At a later date a somewhat similar method of preparation was employed on the large scale, and the product was termed *Corrosive sublimate* or *Mercurius sublimatus corrosivus*. For this purpose an intimate mixture of 3 parts of mercury, 2 of common salt, 2 of saltpetre, and 4 of calcined ferrous sulphate was heated:—

$$Hg + 2NaCl + 2KNO_3 + Fe_2S_2O_9 = HgCl_2 + Na_2SO_4 + K_2SO_4 + Fe_2O_3 + 2NO_2.$$

The nitrogen peroxide which was given off was condensed in water, and the acid obtained employed for the preparation of mercuric oxide. At the end of the sixteenth century, corrosive sublimate was a well-known commercial article. In the works of the so-called Basil Valentine the following statement occurs. He says: "Recipe mercurii sublimati, such as can be bought at the druggists, and has been sublimed with vitriol and salt; for the ☿ takes up in the sublimation the quintam essentiam salis. Then rub down the mercurium sublimatum very finely, lay it in the cellar in a thin layer on an iron plate, let it lie for some days and nights, when a fluid will be seen to flow from it, and the ☿ is revivified."

From its strongly corrosive properties, mercuric chloride was also termed *Draco*, and as it was capable of destroying the metallic lustre of several metals, it was called *mors* or *malleus metallorum*. The process which is now employed for the manufacture of corrosive sublimate, namely, that of subliming a mixture of mercuric sulphate and common salt, was first suggested by Kunkel, who in the year 1760 described this process in his *Laboratorium Chymicum* as follows: "The best *mercurius sublimatus* for use in chemistry and such as pleases me, is when I take an oleum vitrioli, which has been highly freed from all its

phlegm, with merc. viv. ana, or if it has not been rectified so well, merc. one part and oleum one and a half parts, and distil off so much oleum until all the merc. is coagulated. This white Praecipitat sublimed with Sal communis ana gives a fine corrosive sublimate."

Mercuric chloride is obtained commercially by heating a mixture of equal parts of dry common salt and mercuric sulphate. As the latter salt can only with difficulty be got free from mercurous salt, one-tenth of its weight of manganese dioxide is added to the mixture in order to prevent formation of calomel. The sublimation is carried on in large, flat, long-necked glass balloons, which are first placed in a sand-bath up to their necks, and gently heated in order to drive off all moisture. So much of the sand is then removed that only the lower half of the balloon is surrounded by sand, and then this is heated more strongly until the whole of the chloride is sublimed. On cooling, the balloon is broken and the cake of sublimate removed.

Mercuric chloride crystallises in needles belonging to the rhombic system,[1] the commercial article usually having the form of a semi-transparent crystalline crust. According to the experiments of Poggiale, 100 parts of water dissolve the following:—

At	10°	20°	50°	80°	100°
$HgCl_2$	6·57	7·39	11·34	24·3	53·96

Mercuric chloride dissolves in about three parts of alcohol crystallising from the solution in colourless asymmetric needles, and in four parts of ether, so that when this liquid is shaken up with the aqueous solution, the greater part of the salt is removed from the water. It crystallises by sublimation in a second asymmetric form.[2] It also dissolves without decomposition in concentrated sulphuric and nitric acids. Its specific gravity is 5·403 (Karsten), it melts at 288° and boils at 303°, the specific gravity of its vapour being 9·8 (Mitscherlich), corresponding to the normal molecular weight. Corrosive sublimate possesses a sharp metallic taste, and is a violent poison, and it is largely used, both externally and internally, in medicine, especially in cases of syphilis. It is also used as an anti-putrescent

[1] Mitscherlich, *Pogg. Ann.* 1833, **28**, 118.
[2] Von Lang, *Wien. Acad. Ber.* 1862, **45**, 119.

for anatomical preparations, and in dressing furs and skins, and especially as a bactericide in antiseptic surgery.

Mercuric chloride has the power of forming crystallisable compounds with a number of other chlorides, especially with the chlorides of the alkali-metals, giving rise to the following double chlorides :—

$KCl + HgCl_2 + H_2O$	$2NaCl + 2HgCl_2 + 3H_2O$
$2KCl + HgCl_2 + H_2O$	$NH_4Cl + HgCl_2$
$KCl + 2HgCl_2 + 2H_2O$	$2NH_4Cl + HgCl_2 + H_2O$
$2NaCl + HgCl_2$	$2NH_4Cl + 3HgCl_2 + 4H_2O$

The fact that these salts dissolve in water more easily than mercuric chloride has long been known. The iatro-chemists prepared one of them by dissolving equal parts of corrosive sublimate and sal-ammoniac, and crystallising the solution. It was termed by them *Alembroth*.

Mercuric chloride dissolves in hydrochloric acid of specific gravity 1·158, when slightly warmed. On cooling, a crystalline mass of the compound $HgCl_2 + HCl$ is deposited, whilst on strongly heating the solution the compound $2HgCl_2 + HCl$ is formed. Both lose hydrochloric acid on exposure to the air (John Davy).[1]

When mercuric chloride is heated from 200° to 220° with phosphorus pentachloride, the compound $3HgCl_2.2PCl_5$ sublimes in fine glistening needles, which melt readily. The same compound is formed when calomel is heated with phosphorus pentachloride :

$$7PCl_5 + 6HgCl = 2\ (3HgCl_2.2PCl_5) + 3PCl_3.$$

Mercuric chloride also forms a series of basic salts or *oxy-chlorides*, which are obtained by the action of mercuric oxide on mercuric chloride solution, or by adding potassium hydrogen carbonate to the latter. The best defined of these are $2HgCl_2 + HgO$, which crystallises in monosymmetric needles ; $HgCl_2 + 2HgO$, which is a pitch-black crystalline precipitate, and $HgCl_2 + 3HgO$, which forms glistening golden-yellow scales. In addition to these, several other oxy-chlorides are known containing a larger amount of oxygen.

Mercuric Bromide, $HgBr_2$. Mercury combines with bromine with evolution of heat, and the oxide dissolves in hot aqueous

[1] *Phil. Trans.* 1822, 357.

hydrobromic acid. The bromide crystallises from aqueous solution in glistening scales, melting at 244°,[1] and from alcoholic solution in rhombic needles or prisms, which can easily be sublimed.

Mercuric Iodide, HgI_2, is formed when the two elementary constituents are rubbed together in a mortar with a small quantity of alcohol. It forms a scarlet crystalline powder. It is also precipitated when a solution of potassium iodide is added to one of corrosive sublimate. In this case, however, the precipitate which first forms has a pale yellow colour, but soon becomes scarlet; it is easily soluble in an excess of either liquid. Mercuric iodide crystallises in quadratic prisms and pyramids, from solution in hot, moderately concentrated solution of iodide of potassium, in boiling alcohol, or in hot nitric acid. It melts at 253—254°, and volatilises without decomposition, the vapour having the density 15·6—16·2, corresponding to the formula HgI_2. It is very slightly soluble in water, but dissolves in many aqueous acids, ammoniacal salts, salts of mercury, and soluble iodides, with which it forms soluble double compounds.

Mercuric iodide is dimorphous, for on gently heating the red modification to a temperature of 150° the mass becomes yellow. This change also takes place when the red crystals are melted or sublimed, yellow rhombic prisms being formed. These readily pass into the red modification when touched or rubbed with a hard body, and even spontaneously, heat being evolved, and the red crystals retaining the form of the yellow.

When a cold solution of corrosive sublimate and then water is added to an alcoholic solution of potassium tri-iodide (KI_3) heated to 50°, a brown crystalline precipitate is obtained of *mercury periodide*, HgI_6. If both solutions be mixed together hot, and allowed to cool slowly, rhombic tables of mercury periodide are obtained mixed with the yellow and red iodide. Mercury periodide possesses in a high degree the peculiar optical properties of tourmaline (vol. i. p. 873), and readily loses iodine.

267 *Mercuric Sulphide* or *Cinnabar*, HgS, usually occurs in beds in slate rocks and shales, and more rarely in granite or porphyry. It is found in Idria, Almaden, in the Palatinate, in Carinthia, Transylvania, Tuscany, in the Urals and Altai, in China abundantly, and in Japan, Mexico, and Southern Peru. Extensive mines of cinnabar exist in California in the coast

[1] Carnelley and Williams, *Journ. Chem. Soc.* 1880, i. 127.

ranges at different points, at Clear Lake in the North to San Louis Obispo in the South, the principal mines in which region are at New Almaden and the vicinity in Santa Clara Co., about sixty miles S.S.E. of San Francisco.

Cinnabar is found in rhombohedral crystals, which, like quartz, cause the circular polarisation of light, and also in the granular and massive states. It possesses a cochineal-red colour often inclined to brownish-red and lead-grey; its streak is scarlet, and it is sub-transparent or opaque, possesses a conchoidal fracture and adamantine lustre. Theophrastus mentions this mineral as *κιννάβαρις*; the term, however, was afterwards used to designate dragons' blood. Pliny terms this latter substance *cinnabaris*, and the mineral cinnabar, being frequently confounded with red-lead, is termed by him *minium*.

The artificial preparation of this compound was first described by the Latin Geber under the name of *usifur*. At the beginning of the seventeenth century, Turquet de Mayerne found that by rubbing mercury and sulphur together a black powder was obtained, and in 1689 Walter Harris showed that this compound could be obtained by intimately mixing dry sulphur and mercury. Prepared in this way it was termed *Æthiops mineral*, and was employed as a medicine, and in the year 1757, J. C. Jacobi proposed to employ for the same purpose the precipitate obtained by adding caustic soda to a solution of a mercury salt; this was known under the name of *pulvis hypnoticus*. The mode of preparing cinnabar by the wet way was first observed by G. Schulz, in 1687; he obtained it by shaking together for some time, Boyle's volatile tincture of sulphur and metallic mercury. In 1773, Baumé showed that the black precipitate which this liquid produced in a solution of mercury was gradually converted into cinnabar. The difficulty of explaining the difference between the black and the red sulphides of mercury was increased by the fact that the one could be converted into the other. Stahl believed that the black compound contained more sulphur that the red one; others assumed that in the latter compound the sulphur was more intimately combined than in the former, or that both being compounds of oxide of mercury with sulphur, the cinnabar contained mercury in a higher state of oxidation. Berthollet, on the other hand, considered cinnabar as mercury sulphide, whilst he regarded the black modification as a compound of mercury with sulphuretted hydrogen. It was not until 1833 that the identity

in composition of both these substances was ascertained by Fuchs,[1] and the difference between them explained by the fact that the black compound was amorphous whilst the red was crystalline.

In order to prepare cinnabar in the dry way, according to the Dutch process, mercury is added to an excess of fused sulphur and the cold broken mass brought into earthenware pots which are heated in a sand-bath until the excess of sulphur is driven off. The crucible is then covered with an iron plate and the temperature raised until the cinnabar sublimes and is deposited upon the plate.

In the process of manufacturing vermilion in Idria, 8 parts of sulphur and 42 parts of mercury are placed in small barrels which are caused to rotate on their axes until the contents are converted into a brown powder; this substance is then distilled in iron retorts, furnished with a head and receiver; the purest cinnabar condenses in the head of the retort whilst the portions deposited in the receiver consist of a mixture of this substance with sulphur and require redistillation. The sublimate is then very finely levigated, treated with caustic soda, and then washed with water and dried.

Vermilion obtained in the wet way possesses a much finer colour than the sublimed vermilion, and it can be prepared in a variety of ways. According to Brunner's[2] process 100 parts of mercury and 38 parts of flowers of sulphur are rubbed together for some hours and then the mass mixed with 25 parts of potash dissolved in 150 parts of water at 45°. The mixture is then heated, the quantity of water being kept constant for about eight hours. After this time the mass begins to exhibit a red colour, and when the right tint has been attained the mass is quickly washed with water, as by the further action of potash the vermilion becomes brown. In another process described by Firmenich,[3] 5 kilos of mercury mixed with 2 kilos of sulphur and 4·5 liters of a solution of potassium pentasulphide are heated in a water-bath, the potassium pentasulphide solution being obtained by reducing 20 parts of potassium sulphate with carbon and boiling the product with 3·5 parts of water and 15 parts of sulphur. The mixture is then poured into strong stoppered bottles and these are well shaken whilst the liquid is being heated. After the lapse of from three to four hours a

[1] *Schweigg. Journ.* **67**, 1864.
[2] *Pogg. Ann.* 1828, **15**, 593.
[3] *Dingl. Polyt. Journ.* 1864, **172**, 370.

brown powder is formed. The liquid is then allowed to cool to 50° and is digested at this temperature for some days until the colour of the product reaches the right shade; then it is mixed with caustic soda in order to withdraw the excess of sulphur, washed with water, and dried at 60°.

Sublimed cinnabar is often observed in distinct crystals, having the form of the natural mineral. Generally, however, it forms a fibrous mass, having a cochineal-red colour, but when powdered it has a scarlet-red tint. Its specific gravity is 8·124 (Boullay); the specific gravity of its vapour is 5·34 (V. Meyer), from which it appears that in the gaseous condition the compound undergoes dissociation. Cinnabar is not attacked by hot nitric acid, but aqua-regia dissolves it easily with liberation of sulphur. It is soluble in concentrated hydriodic acid in the cold and also in the dilute acid when warmed, sulphuretted hydrogen being evolved (Kekulé). Vermilion is used as an oil- and water-colour paint, for red lithographic- and printers'-ink, and for colouring sealing-wax, &c. It is sometimes adulterated with red-lead or red oxide of iron. The presence of these impurities can be readily ascertained, inasmuch as pure vermilion sublimes without leaving any residue.

Black or amorphous mercuric sulphide, which occurs as a mineral in California,[1] is formed, as has already been stated, when flowers of sulphur and mercury are mixed together. The excess of sulphur can be removed by carbon bisulphide, and the excess of mercury by dilute nitric acid. It is likewise formed when the component elements are gently heated together, and also by gently heating cinnabar in absence of air, although by the application of a stronger heat the latter compound again sublimes. When solutions of the polysulphides of the alkali metals act upon mercury, the black sulphide is likewise obtained, and the same compound may also be prepared by acting with an excess of sulphuretted hydrogen or sulphide of ammonium on a solution of a mercuric salt. Mercurous salts treated in this way yield a mixture of mercuric sulphide and finely-divided mercury. On passing sulphuretted hydrogen into a solution of mercuric chloride, a white precipitate is first obtained, and this becomes yellow and ultimately black by the further action of the gas. This white compound has the composition $2HgS + HgCl_2$, and on sublimation decomposes into

[1] Moore, *J. Pr. Chem.* 1870 [2], **2**, 319.

cinnabar and corrosive sublimate. Other salts of mercury form similar compounds.

Mercuric sulphide also combines with the sulphides of the alkali metals; thus, for instance, if a solution of mercuric chloride be treated with a solution of potassium sulphide containing some free alkali, a clear solution is obtained and, on evaporation, very slender silky needles of the compound $HgS + K_2S + 5H_2O$ are deposited. It is a very unstable compound, and on washing is resolved into its constituents. It was first obtained by Brunner, in the preparation of vermilion according to his method. The conversion of the black amorphous sulphide into vermilion, probably depends upon the formation of this body.

Mercuric Sulphate, $HgSO_4$.—This salt was known in the fourteenth century, and is obtained by heating mercury with oil of vitriol. In order to prepare a product free from mercurous salt, the mercury must be heated with 1·5 times its weight of sulphuric acid, and evaporated to dryness. In this way a white opaque mass is obtained, which crystallises from an excess of sulphuric acid in small stellated plates, having a silvery lustre. When gently warmed it becomes yellow and afterwards red-coloured, and decomposes, when strongly heated, into mercury, oxygen, sulphur dioxide, and mercurous sulphate. Boiling water decomposes it into a soluble acid salt and the insoluble basic salt, Hg_3SO_6, a heavy lemon-coloured powder which on heating becomes of a red colour, dissolves in 2,000 parts of cold, and 600 parts of boiling, water. This basic compound was described by Basil Valentine, and was used by the iatro-chemists under the name of *turpetum minerale.*

268 *Mercury Nitride* or *Trimercuric-diamine,* N_2Hg_3.—This compound may be considered as derived from a double molecule of ammonia, N_2H_6, by the substitution of three atoms of dyad mercury in the place of six atoms of hydrogen. For its preparation, ammonia gas is passed over dry precipitated mercuric oxide, first in the cold and afterwards at a temperature of 130° until no further formation of water occurs:[1]

$$3HgO + 2NH_3 = N_2Hg_3 + 3H_2O.$$

The dark brown powder which is thus obtained is treated with dilute nitric acid in the cold in order to extract any mercury or

[1] Plantamour, *Annalen,* 1841, **40,** 115.

mercuric oxide. In the dry state trimercuric-diamine explodes with great violence on heating, on friction, on percussion, or in contact with strong sulphuric acid. Alkalis decompose it, ammonia being evolved.

Mercuric Nitrate, $Hg(NO_3)_2$.—This salt was classed among the vitriols by the alchemists, and its preparation is thus described in the works of Basil Valentine:

"Vitriolum mercurii is easily made with an *aqua fort* distilled from saltpetre, and alum *ana;* if it is dissolved in it, crystals like a vitriol shoot out; these are then ablued and purified with *spiritus vini*, which previously has been rectified with *sal tartari;* thus it is made into a sweet oil. This is a noble medicine *ad luem gallicam*, it cures all sores, consumptions, disuries, gouts, and drives out many other diseases from the human body."

In order to prepare this salt, mercury is boiled with nitric acid until a portion of the liquid no longer gives a precipitate with common salt. On evaporating the solution over sulphuric acid large crystals, $2Hg(NO_3)_2 + H_2O$, separate out. The same salt, which is very deliquescent, is obtained as a crystalline magma, by adding strong nitric acid to the concentrated solution. The mother-liquor from the large crystals is a thick liquid which has the constant composition $Hg(NO_3)_2 + 2H_2O$. This solution possesses the power, first noticed by Libavius, of colouring the skin a dark-red tint. On evaporating the solution, a basic salt, $2Hg(NO_3)OH + H_2O$, separates out in long transparent prisms which possess a metallic, but not an acid taste. On washing these with water other more basic salts are formed, and at last mercuric oxide remains behind.

Mercuric Phosphide is obtained as a black powder, together with mercuric phosphate, by heating mercuric oxide and phosphorus together in water. If a current of gaseous hydrogen phosphide be passed over gently-heated mercuric chloride, an orange-yellow sublimate of mercuric phosphide is obtained which decomposes into its elements on heating (H. Rose).

269 *Mercuric Carbonates.*—Only basic mercuric carbonates are known. If a solution of mercuric nitrate be poured into an excess of potassium carbonate solution, a dark brown precipitate of H_2CO_3, 2HgO is formed, and if a solution of potassium bicarbonate be employed, an amorphous brown precipitate of $HgCO_3$, 3HgO is formed.

Mercuric Cyanide, $Hg(CN)_2$.—This compound was discovered

by Scheele, who obtained it by boiling Prussian blue with mercuric oxide and water. It is also formed by dissolving mercuric oxide in dilute hydrocyanic acid, or by boiling one part of potassium ferrocyanide with two parts of mercuric sulphate and eight parts of water:

$$2K_4Fe(CN)_6 + 7HgSO_4 = 6Hg(CN)_2 + 4K_2SO_4 + Fe_2(SO_4)_3 + Hg.$$

Mercuric cyanide dissolves in eight parts of cold water and crystallises from the hot aqueous solution in white needles or transparent quadratic prisms which are insoluble in absolute alcohol. Its aqueous solution readily dissolves mercuric oxide, and on evaporating the alkaline solution thus obtained, small needles of a basic cyanide, $Hg(CN)_2HgO$, are formed. Mercuric cyanide is decomposed by hydrochloric, hydrobromic and hydriodic acids, and by sulphuretted hydrogen, with liberation of hydrocyanic acid, but it is not attacked by dilute sulphuric or nitric acids. It forms crystalline double compounds with many other salts. When heated it decomposes into cyanogen and metallic mercury.

Mercuric Cyanate, $Hg(OCN)_2$, and *Mercuric Thiocyanate*, $Hg(SCN)_2$, are white crystalline precipitates. In order to prepare the latter salt a solution of ammonium thiocyanate is precipitated with excess of corrosive sublimate solution. This compound is used for the preparation of the so-called Pharaoh's serpents. The dried precipitate is rubbed up with gum-water to a thick plastic mass, and short cones are formed of this mixture, which are then dried. On igniting them at the end they burn with a blue sulphur-like flame, the ash being very bulky and extending in a serpent-like form.

Ammoniacal Compounds of Mercury.

270 A very large number of different series of ammoniacal derivatives of mercury has been described, but recent researches have shown that only one of these series exists, viz., the dimercurammonium salts, which may be regarded as derived from the ammonium salts by the replacement of the four atoms of hydrogen by two atoms of mercury. The remaining series are either mixtures of these with mercury or mercuric salts or both, or consist of double salts of the dimercurammonium salts

with ammonium salts.[1] Thus the supposed mercurous ammonium derivatives are a mixture of dimercurammonium compounds and finely-divided metallic mercury, which latter gives them a black colour.

Dimercurammonium Oxide, $(NHg_2)_2O$.—When mercuric oxide is gently warmed with pure dilute ammonia, a pale yellow powder having the composition $NHg_2OH + 2H_2O$ is obtained, which deflagrates without explosion on rubbing, or when thrown on to hot charcoal. Heated in a current of dry ammonia to 100° it loses water, yielding the oxide $(NHg_2)_2O$. The anhydrous compound is also formed by the action of dry liquid ammonia on mercuric oxide. It is a dark-brown powder, which on heating or even on trituration, explodes very violently. Dry hydrochloric acid gas decomposes it into mercuric chloride and water. The *hydroxide*, NHg_2OH, is formed when the yellow salt is only heated to 80—85°, and is also a pale brown explosive powder.

Dimercurammonium Chloride, NHg_2Cl, is formed by the action of alcoholic hydrochloric acid on the foregoing compound. It is a yellow powder which, when heated to 300°, is suddenly resolved into calomel, mercury, and nitrogen.

Infusible White Precipitate, which appears to have been first prepared by Lemery, is formed when a solution of mercuric chloride is precipitated by ammonia. It has the empirical formula $NHgH_2Cl$, and appears to be a double salt of dimercurammonium chloride and ammonium chloride, NHg_2Cl, NH_4Cl, as it loses one half of its nitrogen as ammonia on boiling with an alkali. It is a bulky white powder having an earthy metallic taste, and is insoluble in water, but on long-continued washing becomes yellow, owing to the partial removal of ammonium chloride with formation of the yellow dimercurammonium chloride. It decomposes below a red heat without fusion, forming calomel, ammonia and nitrogen:

$$3(NHg_2Cl + NH_4Cl) = 6HgCl + N_2 + 4NH_3,$$

and on warming with ammonium chloride yields the fusible white precipitate, NHg_2Cl, $3NH_4Cl$, described below. If it be mixed with iodine and alcohol poured on to it, mercuric iodide is first formed and then a violent explosion occurs. This mixture also deflagrates in the dry state after some time.

[1] Rammelsberg, *J. Pr. Chem.* 1888 [2], **38**, 558; Barfoed, *J. Pr. Chem.* 1889 [2], **39**, 201; Pesci, *Gazzetta*, 1891, **21**, 569.

Fusible White Precipitate.—This compound was first prepared by Raymond Lully, by precipitating mercuric nitrate with sal-ammoniac and salt of tartar. He was acquainted with its property of fusing when heated. At a later time this body was confounded not only with the foregoing compound, prepared first by Lemery, but also with calomel prepared by the wet process. Kunkel, although he gave both to this last preparation and to fusible white precipitate the name of *lac mercurii*, was aware of their difference. He says, "Whether these two have the same effect in medicine, I leave to the physicians and surgeons; *in examine chymico* they are very different." Wöhler, in 1838, pointed out the difference between the fusible and infusible precipitate.

Fusible white precipitate is obtained either by adding a solution of corrosive sublimate to a boiling aqueous mixture of sal-ammoniac and ammonia as long as the precipitate which is formed dissolves, or by boiling the infusible white precipitate with a solution of sal-ammoniac. Small regular dodecahedra or crystalline crusts are deposited on cooling. It has the empirical formula $N_2HgH_6Cl_2$, and probably consists of the double salt NHg_2Cl, $3NH_4Cl$, as on boiling with an alkali it loses three-quarters of its nitrogen as ammonia, this supposition also agreeing with its formation from infusible white precipitate and ammonium chloride. The compound fuses on heating, losing nitrogen and ammonia, whilst a mixture of calomel, corrosive sublimate and sal-ammoniac sublimes.

Dimercurammonium iodide is obtained by the action of liquid ammonia on the compound HgI_2, $3HgO$, or by neutralising the oxide with hydriodic acid. After drying at 130° it forms a brown powder, which explodes on further heating. The *monohydrate* $NHg_2I + H_2O$, which is frequently described as oxydimercurammonium iodide, NH_2Hg_2OI is formed by the action of an excess of ammonia on mercuric iodide, and also when ammonia is passed at a temperature of 180° over the basic oxyiodide of mercury, HgI_2, $3HgO$.

The same compound is easily obtained by adding ammonia to a solution of mercuric potassium iodide, containing an excess of potash, and hence this liquid, known as Nessler's solution (vol. i. p. 301), is employed as a very delicate reagent for the detection of ammonia. The hydrate is a brown powder which often exhibits a reddish-purple colour, and, on heating in absence of air, fuses to a brown liquid, whilst when more strongly heated, it

decomposes with emission of light, into water, mercuric iodide, ammonia, and nitrogen.

Dimercuriphosphonium compounds analogous to the above dimercurammonium salts have also been prepared.

Therapeutic Uses of Mercury and its Compounds.

Liquid mercury appears to be destitute of poisonous properties, many instances having occurred in which it has been swallowed without any evil effects following. In a finely-divided state, and in the state of vapour, however, metallic mercury acts as a poison, and its salts are poisonous.

In some respects the poisonous action of mercury compounds resembles that of the salts of other heavy metals, but they also act on the animal economy in a special manner, rendering them of great therapeutic value. Metallic mercury is employed, in a very finely divided state, both internally and externally. It acts on the one hand upon the glandular secretions, especially upon the salivary glands, whilst on the other it affects the nervous system. Taken continuously, it produces salivation, ulcers of the mucous membrane of the mouth, and paralysis. Mercury and certain of its compounds are employed both for local and general inflammation, being especially valuable in cases of syphilis. Of the salts of mercury, the two chlorides, calomel, HgCl, and corrosive sublimate, $HgCl_2$, are most generally employed. Calomel does not appear to undergo any change in the stomach, but seems to be altered in the bile secretion, by which it is taken up into the system. In large doses it acts as a poison; in smaller doses (from 0·1 to 0·4 grm.) as a purgative, and in small doses, especially when continued, it appears to act as the metal does. Corrosive sublimate is a powerful caustic poison, producing vomiting, colic, diarrhœa, and great weakness. It is used in very small doses in cases of syphilis, as it does not so readily produce salivation as the other mercurial preparations.

Mercury is not a cumulative poison, as the larger portion is quickly excreted from the body soon after it has been taken, and may be found in the excrements as well as in saliva or pus. It is, however, difficult to remove the last traces from the system, and chronic mercurial poisoning is common with those who habitually work with the metal, such as manufacturers of mirrors,

barometers, &c. The poisonous effects of mercury were known to Dioscorides and Pliny, and it appears that even in those days it was employed as a medicine. From that period up to the fifteenth century, mercury was but sparingly used in medicine, and then for external purposes only. Even in the fifteenth century the outward use of mercurial compounds was discountenanced by the then prevailing schools of medicine, and at the beginning of the sixteenth century the few physicians who had dared to employ mercurial ointment were vigorously assailed. The employment of mercurial preparations was, however, soon afterwards introduced by Paracelsus, and by degrees became common.

Detection and Estimation of Mercury.

272 Bunsen's flame-reaction may be conveniently employed in order to detect the presence of mercury in a solid body. For this purpose the substance is mixed with a small quantity of anhydrous sodium carbonate and nitre, and the mixture is heated in a tube held in the flame by means of a platinum wire wound round it, the mouth of the tube being placed directly under a small porcelain basin filled with cold water. The mercury is then volatilised, and condenses on the cool lower surface of the porcelain basin in the form of a grey film. This is wiped off with a small piece of filter paper, when the minute globules of liquid metal are rubbed together and a larger globule is obtained. If a large quantity of mercury be present, globules are at once formed on the cold basin.

A similar film can be more simply obtained by heating the compound on a piece of asbestos in the reducing zone of the flame beneath a porcelain basin. The metal may also be detected by heating the compound in a bulb tube with sodium carbonate and potassium cyanide, the mercury being deposited on the cool part of the tube.

When a liquid has to be tested for mercury, it is in the first place acidified with hydrochloric acid. If this produces a white precipitate a mercurous salt may be present together with silver, lead and thallium. The two last metals may be removed by boiling the precipitate with water. The residue is then treated with ammonia, in which the chloride of silver is soluble. If a black powder remains mercury is present, and its presence can be confirmed by the flame reaction just

described. The filtrate from the first precipitate, or the solution in which the hydrochloric acid gives no precipitate, is saturated with a current of sulphuretted hydrogen gas. If mercury be present a white precipitate will first be formed, but this rapidly changes colour, becoming yellow, brownish-red, and finally black. In order to separate mercury from the other sulphides which may be present, the precipitate is first washed with hot water, then warmed with sulphide of ammonium, again washed with water, and the residue treated with hot dilute nitric acid. If a heavy black powder remains undissolved, this is treated with aqua-regia, the solution concentrated, and tin dichloride added to this solution, when calomel is precipitated, and if an excess of the precipitant be added, finely-divided metallic mercury is deposited as a black powder, which on boiling with hydrochloric acid unites to form distinct globules. The following equations represent the decomposition:

(*a*) $2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$.
(*b*) $2HgCl + SnCl_2 = 2Hg + SnCl_4$

The spark-spectrum of mercury obtained by an electric discharge passing from platinum wires moistened with mercuric chloride contains several lines, of which one in the green almost coincident with a silver line, and one in the blue are especially bright. In addition to these there are two other characteristic lines close together, occurring in the greenish yellow (Lecoq de Boisbaudran).

Mercury is best determined quantitatively by precipitating the solution with sulphuretted hydrogen. The sulphide thus precipitated frequently contains free sulphur, and it is therefore warmed with hydrochloric acid, nitric acid being added drop by drop until the sulphur, which separates out, has become yellow. Then the solution is diluted with water, nearly neutralised with caustic soda, excess of potassium cyanide added, and the sulphide again thrown down with sulphuretted hydrogen; the precipitate thus obtained is quickly washed with cold water, dried at 100° and weighed. The sulphur may also be removed by washing the precipitate with alcohol to remove water, and then with carbon bisulphide. Mercury is also sometimes estimated in the form of mercurous chloride or as the free metal.

Atomic Weight of Mercury.—The atomic weight of mercury was determined by Turner,[1] and by Erdmann and Marchand,[2]

[1] *Annalen*, 1835, **13**, 14. [2] *J. Pr. Chem.* 1844, **31**, 385.

by the analysis of mercuric oxide, and also by the latter investigators by the analysis of the sulphide. Millon[1] and Svanberg[2] estimated the quantity of mercury formed by heating the chloride with lime in a current of hydrogen. The numbers obtained by the various investigators agree well together, the average of the most reliable results being 198·9 (O=15·88).

GROUP III.

Sub-Group (*a*).—Boron and the Rare Earth Metals.

Boron.
Scandium.
Yttrium.
Lanthanum.

Sub-Group (*b*).—The Aluminium Group of Metals.

Aluminium.
Gallium.
Indium.
Thallium.

273 These elements all form oxides of the formula R_2O_3 and unite with the halogens to form compounds of the type RX_3 or R_2X_6.

Boron hydroxide behaves as an acid to most bases and only acts as a base towards the strongest acids, but the basicity of the oxides increases with the atomic weight of the metal. The oxides of the metals of sub-group (*a*) are, as in the second group, more basic than those of sub-group (*b*). Thus the latter form salts with strong alkalis, whereas the former do not.

The element boron has already been described among the non-metals (vol. i. p. 640). Since the chemical relations of the rare earth metals are so little known at present, the metals of sub-group (*a*) are described along with the other rare earth metals.

[1] *Compt. Rend.* 1845, **20**, 1291. [2] *Jahresb.* 1847-8, 445.

THE ALUMINIUM GROUP.

Aluminium. Gallium. Indium. Thallium.

274 These metals are permanent in the air at ordinary temperatures, but become oxidised when strongly heated in air or oxygen. The volatility of the metals increases with the atomic weight, and the same order is observed in the case of reduction from the oxide. Thus indium and thallium both yield an incrustation of the oxide and a metallic bead, when their compounds are reduced on charcoal, whereas aluminium compounds do not show this reaction.

All these metals have small atomic volumes and occur just after the minima on Lothar Meyer's diagram (p. 55). They are all malleable and fusible, and form typical hydroxides which act as weak bases, the corresponding salts being often readily decomposed by boiling with water. These hydroxides also act as weak acids towards strong bases. Thus the hydroxide of gallium is soluble both in potash and ammonia, and those of aluminium and indium in potash, whilst thallic hydroxide is insoluble in alkalis.

Aluminium, gallium and indium form characteristic double sulphates of the formula $M'_2SO_4 + R_2(SO_4)_3 + 24H_2O$, known as the alums, in which M′ represents a monovalent metal (p. 556). Similar compounds have not yet been obtained from thallium. Both aluminium and thallium yield organo-metallic derivatives.

Special interest attaches to the position of gallium in this group, because its properties and relations to aluminium and indium show that it is identical with the "eka-aluminium" of Mendeléef, the existence of which was predicted by that chemist four years before the actual discovery of the element by Lecoq de Boisbaudran (p. 61.)

In addition to compounds of the type RX_3, lower chlorides of indium and gallium are also known, whilst thallium forms a whole series of salts in which it acts as a monovalent metal. These salts are more stable than those which correspond in type to the aluminium salts and bear a remarkable chemical resemblance to the salts of the alkali metals. Physically the metal thallium closely resembles lead which occupies the corresponding place in Group IV., and its compounds with the halogens (except fluorine) and sulphur are very similar in properties to the corresponding lead compounds. In consequence of this remarkable

behaviour, Dumas, on the occasion of the discussion of Lamy's investigation in the French Academy, termed it the ornithorhynchus amongst the metals.

ALUMINIUM Al = 26·9.

275 The name of this metal is derived from *alumen*, alum. This, as well as the corresponding Greek word (*στυπτηρία*), was originally used to designate very different bodies, all of which possessed the common property of an astringent taste. There can, however, be little doubt that alum itself was included amongst these bodies, and this salt was well known to the Latin Geber and the later alchemists, being, however, classed amongst the vitriols, until Paracelsus showed that it differed from this last family of salts. In his second treatise, *De Generibus Salium*, he states: "Alum is in no wise connected with the metals, but is a salt, standing alone in the acid, and taking its *corpus* from the intermixture of the earths; vitriol does not do so, but solely from the intermixture of metallic *corpora*." The nature of the earth, which is combined in alum with sulphuric acid, remained long undetermined. It was usually supposed to be a calcareous earth, although it was noticed in the seventeenth century that clay, when treated with sulphuric acid, gave an alum; and hence Pott, in his *Lithognosy*, published in 1746, stated that the basis of alum was an argillaceous earth. It was not till 1754 that Marggraf showed that alumina differed totally in its properties from lime, and that clay contained this earth, combined with silica.

Davy, as well as other chemists, endeavoured to decompose alumina into its elements, as it was generally acknowledged to be an oxide. The results they obtained were, however, but unsatisfactory, and Wöhler, in 1827, was the first to prepare pure aluminium.

Of all the elements, with the exceptions of oxygen and silicon, aluminium is the most widely distributed, and contained in the largest quantity in the solid crust of the earth. It occurs as the oxide, Al_2O_3, in the mineral corundum, of which the ruby and sapphire are varieties. It is found more commonly as diaspore, $Al_2O_4H_2$, and bauxite, $(Al_2,Fe_2)O_5H_4$, whilst it occurs in far larger quantity in combination with silica, forming a great variety of double silicates, amongst which potash-felspar or orthoclase,

$(K,Na)AlSi_3O_8$, may be mentioned as being most important, as this forms the chief constituent of granite, gneiss, syenite, porphyry, trachyte, &c. Soda-felspar, or albite, and lime-felspar, or labradorite, also occur in large quantities. Amongst other important double silicates we find the garnet group. The several members of this group are named from the different isomorphous metals which they contain; thus, for instance, we have lime-alumina garnet or grossular, $Ca_3Al_2(SiO_4)_3$; iron-alumina garnet, or almandite, $(Fe,Mg)_3Al_2(SiO_4)_3$; lime-iron garnet, or andradite, $Ca_3Fe_2(SiO_4)_3$. The group of micas also contains a large number of important minerals, as common mica or biotite, $K_2HAl_3(SiO_4)_3$, $(Mg,Fe)_6(SiO_4)_3$; and chlorite or ripidolite, $H_9(Fe,Mg)_5Al_3Si_3O_{20}$, the latter compound forming the chief constituent of many slate rocks.

Aluminium also occurs in large quantities as cryolite, double fluoride of aluminium and sodium, Na_3AlF_6, the name being derived from the ice-like appearance of the mineral, which is largely worked in Greenland and serves as an industrial source of the metal.

The weathering of felspar gives rise to porcelain-clay, china-clay, or kaolin, $Al_2Si_2O_7 + 2H_2O$, whilst the different varieties of coloured clays are obtained from a similar disintegration of felspathic rocks containing iron.

Although alumina is largely contained in all fertile soil, it is only found in small quantity in most plants.[1] Certain cryptograms, however, especially the species of lycopodium, take it up largely. Thus the ash of *L. Clavatum* contains up to 26·65, and that of *L. Chamaecyparissus* even as much as 57·26 per cent. of alumina.[2] Aluminium is also contained in the solar atmosphere.

276 *Preparation of Metallic Aluminium.*—The process which Wöhler used for the preparation of aluminium is one which may be employed for the preparation of all those elements which occur in nature combined with oxygen, and whose oxides are not reducible either in the presence of carbon or of hydrogen. It consisted[3] in fusing together potassium and chloride of aluminium in a closed crucible. The metal was thus obtained in the form of a grey powder, which, under the burnisher, exhibited a metallic lustre, and when pressed in an agate mortar adhered together in the form of glittering particles.

[1] Yoshida, *Journ. Chem. Soc.* 1887, i. 748; Berthelot and Andrée, *Compt. Rend.* 1895, **120**, 288.

[2] Aderholdt, *Annalen*, 1852, **82**, 111.

[3] *Pogg. Ann.* 1827, **11**, 146.

Wöhler afterwards improved his method, and, by passing the vapour of aluminium chloride over potassium, obtained the metal in fused globules.[1] In the year 1854 Bunsen[2] prepared aluminium by electrolysis of the chloride, and in the same year Deville commenced his first experiments on the preparation of aluminium on a large scale. The process he employed was that of Wöhler, potassium being, however, replaced by sodium, and he found that instead of the pure chloride it was preferable to use the double chloride of aluminium and sodium. In the Paris Exhibition of 1855 the "silver made from clay" naturally attracted great attention. Deville then, in concert with other chemists, extended his experiments, and with their help the process was still further improved, and aluminium was first prepared on the large scale at works near Alais, under the direction of M. Merle.

Pure aluminium hydrate (p. 549) was made into balls with common salt and coal-dust and the mixture exposed at a white heat to a current of chlorine, by the action of which the volatile double chloride of sodium and aluminium, $NaCl,AlCl_3$, was produced. The latter was then heated with metallic sodium and a flux and the aluminium run into moulds.

Electrolytic Production of Aluminium.—The above method for the preparation of the metal has now however been entirely superseded by an electrolytic process. Instead of electrolysing fused sodium aluminium chloride, a fused mixture of cryolite and common salt was substituted for the chloride by Bernard Bros., of Paris, who from 1887 manufactured the metal in this manner. In America the brothers Cowles succeeded in producing aluminium bronze by acting on alumina with carbon at the temperature of the electric furnace in the presence of metallic copper, but this method has now been replaced by the modern electrolytic processes. The present manufacturers employ as their starting-point pure anhydrous alumina. In the Hall process which is employed at Pittsburgh and Niagara, this is dissolved in a bath of fused cryolite, and fluorspar or some similar fluoride, which is contained in an iron pot lined with carbon, and is kept melted by the electric current, the temperature of the bath being about 980°. A bundle of carbon rods is used as the anode, whilst the pot itself forms the cathode, a current of 7,000 ampères and 6·7 volts being employed. Under these circumstances the alumina is electrolysed and the oxygen

[1] *Annalen*, 1836, **17**, 44, and 1841, **53**, 422.
[2] *Pogg. Ann.* 1854, **92**, 648.

which is liberated combines with the carbon of the anode forming carbonic oxide, whilst the aluminium falls to the bottom of the pot. The fluoride remains unaltered and the process is rendered continuous by periodically adding alumina and withdrawing the metal. The electrical energy required for the production of one pound of aluminium amounts to 3,730 watt-hours.

In the Héroult process, in use at Neuhausen, Foyers and Froges, a similar apparatus is employed, which is shown in plan and section in Figs. 134 and 135. The alumina however is melted without the addition of a flux and is then simply electrolysed.

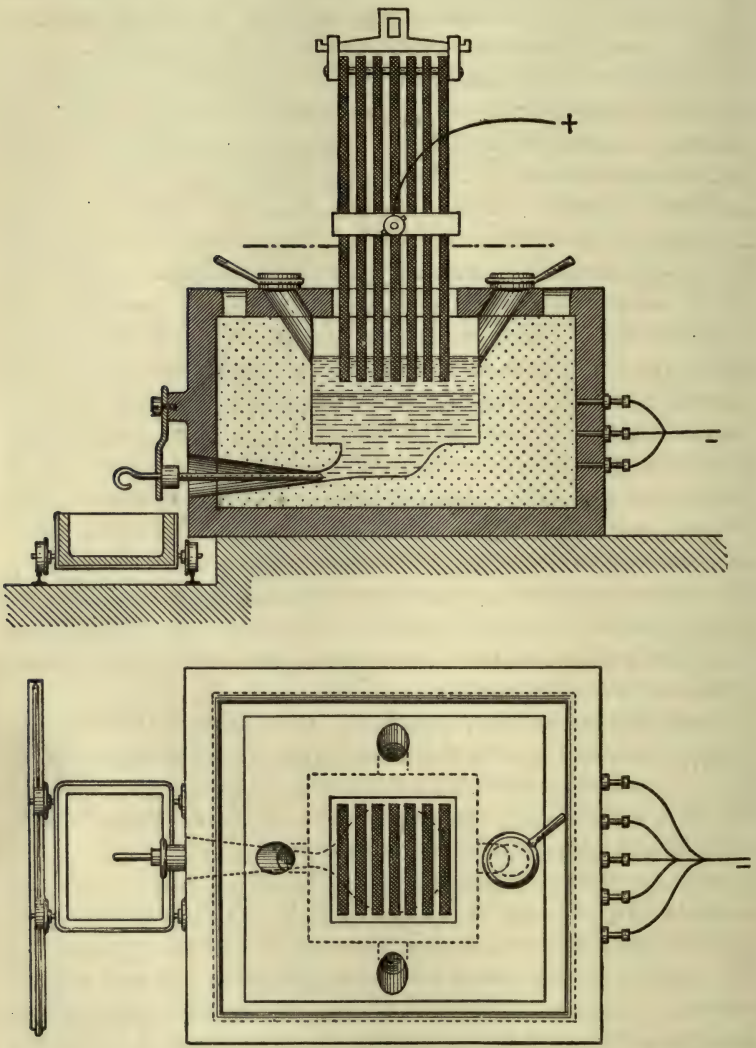
When possible, as at Foyers, Niagara, Neuhausen, &c., water-power, as being cheaper than steam-power, is utilised for the production of the necessary electrical current. Alloys can also be directly made, instead of the metal itself, by carrying out the electrolysis in the presence of the desired metal, which dissolves the aluminium as it is liberated. Manufactured electrolytically, aluminium contains uniformly over 99 per cent. of metal and is very soft and ductile, whilst when made by the sodium-reduction process it usually contained only 97–98 per cent. of metal, and was more brittle and harder to work in consequence of the presence of small quantities of silicon and iron; small amounts of sodium, nitrogen and carbon were also usually present. The annual output of aluminium slowly increased from 1859 to 1888 from one ton to three tons, but from about the latter date the production rose very rapidly, and now reaches many thousand tons per annum.

Pure aluminium was prepared by Mallet[1] from a compound of aluminum bromide with the chlorides of potassium and sodium by heating it with sodium in a crucible lined with a mixture of alumina and sodium aluminate. The product was quite free from silicon, iron, sodium and potassium.

277 *Properties.*—Aluminium is a tin-white metal, which is capable of assuming a bright polish. The appearance of objects made of aluminium is, however, improved by giving to the surface of the metal a dead appearance. This is accomplished by acting on the surface with weak soda-lye, and afterwards washing with dilute nitric acid. Aluminium is malleable, and can be drawn into fine wire and hammered into very thin leaf. It can be best worked at a temperature of 100° to 150°. In the compact state it is very sonorous, emitting a tone when struck like that of flint glass. The cast metal has a specific

[1] *Phil. Trans.* 1880, 1022.

gravity of 2·56, and is as hard as silver, whilst the hammered metal has the hardness of soft iron, and a specific gravity of 2·67. The hardness is again diminished on further heating. It fuses



FIGS. 134 AND 135.

at 654·5°. In order to re-melt the metal a fusing mixture of common salt and potassium chloride must be employed, as the presence of other fluxes, such as borax, glass, &c., renders

the metal very impure. On slowly cooling it assumes a crystalline structure, the forms indicating that it crystallises in octohedra. Its electrical conductivity is 31·7 times that of mercury, whilst its thermal conductivity is 37·3 per cent. of that of silver, and is therefore slightly greater than that of zinc. The specific heat of the metal is 0·214 (Hillebrand), 0·222 (Richards).[1] The tensile strength of aluminium in bars is 28,000 lbs. per square inch, whilst that of a high carbon cast steel is 132,000. Pure aluminium does not oxidise at ordinary temperatures on exposure to air; but the impure metal soon becomes covered with a thin coating of oxide. When heated in oxygen it oxidises only on the surface without combustion. If a fine aluminium wire be wound round a piece of charcoal, the metal burns brightly with the charcoal in oxygen, and if a piece of thin aluminium foil or leaf be heated in a glass globe in an atmosphere of oxygen, it burns with a sudden flash of intensely white light. Aluminium foil decomposes water at 100°, being slowly converted into the hydroxide which retains the form of the foil. The metal dissolves readily in aqueous alkalis, with evolution of hydrogen, and it precipitates the metals lead, silver and zinc from alkaline solutions, whilst neutral or acid solutions are not altered by it. It also precipitates metallic copper from a solution of copper sulphate.

Hydrochloric acid is the best solvent for aluminium. Dilute sulphuric acid, however, also dissolves it slowly with evolution of hydrogen, and concentrated sulphuric acid dissolves it on heating with evolution of sulphur dioxide. On the other hand concentrated, as well as dilute, nitric acid is almost without action on the metal. Organic acids attack it only slightly, but it dissolves in them with ease in the presence of chlorides, such as common salt. Hence it cannot be used for plating cooking utensils. According to Wöhler, aluminium foil takes fire in a current of chlorine, but according to Böttger this is only the case when it is tied round with brass wire to which some Dutch metal is fastened. At high temperatures aluminium also combines with sulphur, selenium, tellurium, phosphorus, arsenic and carbon, and it forms characteristic alloys with many metals.

Aluminium also forms compounds with alcoholic radicals, such as aluminium methide, $Al(CH_3)_3$ and ethide, $Al(C_2H_5)_3$,

[1] *Chem. News*, 1892, **65**, 97; see also Pionchon, *Compt. Rend.* 1892, **115**, 162.

both of which are liquids and are spontaneously inflammable in the air.

Aluminium possesses so many valuable properties, such, for instance, as its low specific gravity, fine lustre, unalterability in the air and in sulphuretted hydrogen, non-poisonous qualities, and ease of working, that a widespread application of the metal was made as soon as the cheaper processes of manufacture lowered the price. Whilst the metal was sold previous to 1886 at £3 per lb., it can now be purchased for half as many shillings.

278 *Alloys of Aluminium.*—Copper forms alloys with aluminium possessing the colour of gold and a very large number of these is in use.[1] That containing about 10 per cent. of the latter metal is usually known as aluminium bronze and possesses the appearance of standard gold. For the preparation of this alloy chemically pure copper must be employed as that which contains iron yields an inferior product. The alloy is at first brittle, but when fused several times it acquires valuable properties. Thus it becomes malleable, yields fine castings, takes a high polish, and has a tensile strength almost equal to that of cast steel. It is now used for the manufacture of physical apparatus as well as of ornamental goods. Aluminium can be alloyed with silver, yielding a hard, easily-polished alloy. That containing 4 per cent. of silver has been employed for the construction of beams for chemical balances, on account of its lightness and its unalterability in the air. Aluminium is also added to iron and steel which are employed for castings.

Alloys of aluminium can be prepared in the way already described and in many cases by adding the oxides, sulphides, or chlorides of the metals to molten aluminium, which reduces the added compound and forms an alloy with its metal.

Aluminium also combines with mercury when it is moistened with caustic alkali, or when the two metals are fused together in an indifferent gas. The amalgam is very brittle, oxidises easily in the air, and decomposes water at the ordinary temperature. The amalgam is also formed when aluminium foil is immersed in a solution of mercuric chloride. It has been employed as a reducing agent[2] for the estimation of nitrates in water and for the preparation of many organic compounds.

[1] Dagger, *J. S. C. I.* 1894, **13**, 4.

[2] Cohen and Ormandy, *Journ. Chem. Soc.* 1890, 811; Wislicenus, *J. pr. Chem.* 1896, **54**, 18.

COMPOUNDS OF ALUMINIUM.

Aluminium and Oxygen.

279 *Aluminium Oxide* or *Alumina*, Al_2O_3, is found in nature as the mineral corundum, crystallising in hexagonal prisms, and of which there are several varieties. The more or less colourless crystals as well as those which are coloured brown by ferric oxide and which are either translucent or opaque are called corundum: those which are coloured red by chromium compounds are termed ruby, whilst those which have a blue tint, due probably to cobalt, are termed sapphires. The yellow crystals are termed oriental topaz, and the purple oriental amethyst, whilst the green are termed oriental emeralds. Coarse and granular corundum containing magnetite or hæmatite intimately mixed with it, and having a grey or blackish colour, is termed emery. Of this mineral there are many gradations, from the finely ground emery to those kinds in which the corundum is present in distinct crystals. Crystallised alumina is excelled in hardness only by the diamond and silicon carbide, and hence it is largely used for polishing and grinding the surfaces of glass and metal.

When aluminium hydroxide or aluminium salts containing volatile organic acids are heated, alumina remains either as a white powder or in amorphous gum-like masses. If this be not too strongly ignited it dissolves in concentrated acids, which however, do not attack the crystallised compound. When more strongly ignited, amorphous alumina becomes denser and harder. After ignition in the flame of the spirit-lamp it has a specific gravity of 3·5, and when more strongly heated in a porcelain-kiln, it attains a specific gravity of 3·9. It is then nearly as hard as corundum but still amorphous (H. Rose). Alumina melts in the oxy-hydrogen flame to a thin liquid, which, on cooling, assumes a crystalline structure and possesses all the properties of corundum. A similar oxide may be obtained by the combustion of the finely divided metal. If aluminium hydroxide be moistened with potassium bichromate and the dried mass fused before the oxy-hydrogen blowpipe, artificial ruby is obtained (Gaudin), and the same material may be prepared by heating to whiteness a mixture of borax and amorphous

alumina containing a small quantity of chromium sesquioxide (Ebelmen). Crystallised alumina is also obtained when fluoride of aluminium is allowed to act upon boron trioxide at a very high temperature (Deville and Caron), when aluminium phosphate is fused with sodium sulphate (Debray), and when alumina is heated to dull redness in hydrochloric acid gas at a pressure of three atmospheres.[1]

Fremy and Feil[2] obtained crystallised alumina on the large scale by heating equal parts of alumina and lead oxide to a bright red-heat. The product consisted of two distinct layers: one of these consisted of lead silicate derived from the action of the lead oxide upon the silica of the crucible; the other was a vitreous mass, and contained cavities filled with colourless crystals of corundum. By the addition of from 2 to 3 per cent. of potassium bichromate to the materials, crystals of ruby were obtained, whilst crystals of sapphire were prepared by adding a trace of oxide of cobalt. Splendid crystals of rose-red coloured ruby were obtained by heating a mixture of equal parts of alumina and barium fluoride with from 2 to 3 per cent. of potassium bichromate to a very high temperature in a glass furnace. This is explained by the production of a volatile fluoride of aluminium which undergoes decomposition in contact with the gases of the furnace with evolution of hydrofluoric acid and deposition of crystalline alumina, the crystals being found in the upper part of the crucible. In these experiments a crystalline double silicate of barium and aluminium was also formed. Artificial ruby and sapphire cannot be distinguished from the natural stones, so that important applications may be predicted for this discovery.

In order to dissolve crystallised alumina it must either be fused together with caustic potash or with acid potassium sulphate. It is also dissolved when heated in closed tubes with concentrated sulphuric acid.

Hydroxides of Aluminium.—Several of these occur in nature. The most important are hydrargillite or gibbsite, $Al(OH)_3$; diaspore, $AlO(OH)$, both of which are crystalline; and bauxite, $(Al, Fe)_2O(OH)_4$, which is found as an amorphous mass.

When ammonia is added to a soluble salt of alumina in the cold, a gelatinous precipitate falls down, but when it is added at the boiling point an opaque white precipitate is deposited,

[1] Haulefeuille and Peney, *Compt Rend.* 1890, **110**, 1038.
[2] *Phil. Mag.* 1878 [5], **5**, 47.

which after drying at the ordinary temperature forms a hard, horn-like mass of the composition $Al_2O_3 + 5H_2O$ or $Al(OH)_3 + H_2O$. When heated to somewhat above 300° it gradually parts with water, forming the compound $AlO(OH)$; and this on ignition yields alumina and water. In this latter reaction the finely divided particles exhibit a peculiar motion which continues even after removal of the flame.[1]

Precipitated aluminium hydroxide possesses in high degree the power of withdrawing from solution both inorganic salts and organic bodies. This property is employed in dyeing.

Moderately ignited alumina readily takes up water with evolution of heat, but does not appear to form any definite compound. The freshly precipitated hydroxide is easily soluble in acids, but the naturally occurring crystallised hydroxides are only attacked by acids after moderate heating. At a bright red-heat they lose the whole of their water and fall with considerable decrepitation into a white powder consisting of the anhydrous oxide. Aluminium hydroxide is usually employed as the source from which the different salts of aluminium are obtained. Its preparation from cryolite has already been described under the alkali-manufacture (p. 213). It is prepared from bauxite by calcining the latter and then heating it with caustic soda solution of specific gravity 1·45 at a steam pressure of 80 lbs. The liquid is then diluted, filtered from the insoluble iron oxide, &c., and allowed to stand in contact with a small amount of precipitated alumina from a previous preparation. Under these circumstances the sodium aluminate is decomposed and alumina deposited, which is then filtered off and washed. The decomposition of the sodium aluminate in presence of aluminium hydroxide seems to depend on the formation of a modification of the latter identical with gibbsite, which is less soluble in caustic soda than the freshly precipitated form.[2] It was formerly the custom to decompose the sodium aluminate by a current of carbonic acid gas, but this has now been abandoned.

Aluminium hydroxide also occurs in two soluble modifications. One of these, which when dried at 100° has the composition $Al_2O(OH)_4 = Al_2O_3 + 2H_2O$ was obtained by Walter Crum[3] by preparing a solution of normal aluminium acetate by the mutual decomposition of lead acetate and aluminium sulphate. This,

[1] Ramsay, *Journ. Chem. Soc.* 1877, ii. 395.
[2] Ditte, *Compt. Rend.* 1893, **116**, 183.
[3] *Chem. Soc. Quart. Journ.* 1854, **6**, 216.

on heating, decomposes with separation of the basic acetate, $Al_2(C_2H_3O_2)_4(OH)_2 + H_2O$, which on treatment for one and a half hours with 200 times its weight of boiling water becomes soluble. If this solution be allowed to stand for ten days and nights at the temperature of boiling water in a closed flask, the acetic acid separates from the alumina. After a sufficient quantity of water has been added to reduce the percentage of alumina to 0·25, the liquid is heated in a flat basin to the boiling point, fresh water being constantly added to replace that lost by evaporation, until all the acetic acid has been driven off. The solution then is perfectly neutral and tasteless, but becomes gelatinous on evaporation.

The second soluble hydroxide of aluminium was obtained by Graham [1] by dialysis of the basic chloride obtained by dissolving the hydroxide in the normal chloride. The normal salt passes through the parchment paper into the water, and a neutral tasteless solution containing alumina remains in the dialyser. This is very unstable, and after some days passes into a jelly. Both these soluble hydroxides are coagulated on the addition of traces of a salt, an acid, or an alkali. Graham's compound acts as a mordant uniting with colouring matters to form lakes, and in the coagulated state is readily soluble in acids. Crum's compound, on the other hand, termed by Graham "meta-aluminium hydroxide," does not combine with colouring matter, and does not dissolve in excess of acid.

Aluminates.—Like other weak bases, alumina acts toward the stronger bases as an acid-forming oxide; thus precipitated alumina dissolves in caustic potash and soda.

Potassium Aluminate, $K_2Al_2O_4 + 3H_2O$, is obtained in hard glistening crystals when alumina and potash are fused together in a silver basin, the solid residue dissolved in water, and the solution evaporated in a vacuum.

Sodium Aluminate, $Na_2Al_2O_4$.—This substance has not been obtained in the crystalline state. It is prepared on the large scale by fusing cryolite with lime, or bauxite with soda or sodium sulphate and carbon, as well as with common salt in a current of steam. When the melted mass is lixiviated with water and the solution evaporated to dryness, sodium aluminate is obtained. As already mentioned its aqueous solution decomposes in presence of aluminium hydroxide. This substance is used as a mordant in dyeing and calico-printing, for the pre-

[1] *Phil. Trans.* 1861, 183.

paration of coloured lakes, and of pure alumina, and for the sizing of paper, &c.

Magnesium Aluminate, $MgAl_2O_4$.—This substance occurs in nature as spinelle. It crystallises in the rhombic system, and is either colourless or variously tinted, and is classed in various species according as either the whole or a part of the magnesium and aluminium is replaced by isomorphous metals. Thus spinelle is $(MgFe)(AlFe)_2O_4$; zinc-spinelle or gahnite is $(ZnFeMg)(AlFe)_2O_4$, &c.

The naturally occurring aluminates were artificially prepared by Ebelmen, by fusing alumina and the corresponding oxide with boron trioxide. This latter substance, which served as a solvent, was almost entirely volatilised at a very high temperature. In this way colourless spinelle was obtained, and this was coloured red by chromium, blue by cobalt, and black by iron; by a similar process the aluminates of barium, beryllium, iron, manganese, &c., can be prepared. Deville and Caron also obtained crystals of gahnite and chrysoberyl by heating aluminium fluoride, together with fluoride of zinc or beryllium, in a carbon crucible which contained a platinum basin filled with boron trioxide.

SALTS OF ALUMINIUM.

280 Aluminium only forms one series of salts, in which one atom of the metal replaces three atoms of hydrogen. Alumina acts as a very weak base and the salts, especially those derived from weak acids, such as acetic acid, are very readily decomposed by boiling their aqueous solutions, a basic salt or the hydroxide being formed.

Many compounds of aluminium are isomorphous with the corresponding compounds of iron, manganese and chromium.

Aluminium and the Halogens.

281 *Aluminium Fluoride*, AlF_3, is best obtained by evaporating to dryness a solution of aluminium in hydrofluoric acid, and subliming the residue, contained in a carbon tube, in a current of hydrogen.[1] It forms transparent, very obtuse rhombohedra,

[1] Brunner, *Pogg. Ann.* 1856, **98**, 488.

which were formerly supposed to be cubes. It is permanent in the air, insoluble in water, and unaltered in the presence of acids and aqueous alkalis; but it is decomposed by long-continued fusion with sodium carbonate. Aluminium dissolves readily in excess of hydrofluoric acid The fluoride forms a series of double fluorides, of which the most important is—

Aluminium Sodium Fluoride, AlF_3, 3NaF.—This occurs as the mineral cryolite at Evigtok, in the Arksutfjord, on the west coast of Greenland, where it forms a bed 80 feet thick and 300 feet long. It was discovered in this locality by Andrada, at the end of the last century. Its mineralogical name was given to it by him inasmuch as it had an ice-like appearance. The investigations of Albidgaard showed that it contained hydrofluoric acid, alumina, and an alkali metal, and Klaproth found the alkali to be soda. The exact composition of cryolite was determined by Vauquelin, Berzelius, and Deville, and in 1849–1850 Julius Thomsen showed that this mineral could be decomposed in the dry way by means of lime and lime salts as well as by the wet way, and upon this observation an important Danish industry was founded. Cryolite usually occurs in masses of a snow-white, reddish, brownish, or bluish colour, which possess easy cleavage; it is found more rarely in asymmetric crystals. When this substance is boiled with milk of lime, or fused with limestone, sodium aluminate, and calcium fluoride are formed. When acted upon with concentrated sulphuric acid it evolves hydrofluoric acid, and the residue contains sodium sulphate, which may be dissolved by the action of cold water, the anhydrous aluminium sulphate, which is formed at the same time, dissolving only in boiling water.

Aluminium Chloride, $AlCl_3$, was first prepared by Oersted by heating a mixture of carbon and alumina in a current of dry chlorine. This method was afterwards adopted and improved by Wöhler,[1] Liebig,[2] Bunsen,[3] and Deville.[4] On the large scale it is prepared in an apparatus similar to that used for the production of the double chloride of aluminium and sodium It may also be readily prepared in a pure condition by heating aluminium in chlorine or in hydrochloric acid gas.[5]

Pure aluminium chloride is a white crystalline solid. It

[1] *Pogg. Ann.* 1827, **11**, 146.
[2] *Pogg. Ann* 1830, **18**, 43.
[3] *Pogg. Ann.* 1854, **92**, 648.
[4] *Compt. Rend.* 1849, **29**, 321.
[5] Nilson and Petterssen, *Zeit. phys. Chem.* 1887, **1**, 459; Stockhausen and Gattermann, *Ber.* 1892, **25**, 3521.

usually possesses, however, a yellowish or greenish colour, due to the presence of ferric chloride and other impurities. It volatilises slowly on heating without fusion, and condenses in hexagonal tablets, but if a large quantity be quickly heated the mass fuses and then boils. When heated in a sealed tube it melts at 194°; the boiling point of the liquid appears to be somewhat below 179°.[1] The specific gravity of the vapour, according to the experiments of Nilson and Petterssen (p. 34), corresponds to the formula $AlCl_3$ at temperatures above 750°.[2] Aluminium chloride is hygroscopic, absorbing water from the air, and emitting fumes of hydrochloric acid. It is also easily soluble in alcohol and ether.

When hydrochloric acid gas is passed into a solution of aluminium chloride in concentrated hydrochloric acid, large hexagonal prisms having the composition $AlCl_3 + 6H_2O$ separate out;[3] these on further heating are easily decomposed into water, hydrochloric acid and residual alumina.

Aluminium chloride absorbs dry ammonia gas, and yields a yellow powder of the composition $AlCl_3 + 3NH_3$. When this is heated in a current of hydrogen the compound $AlCl_3 + NH_3$, soluble in water, sublimes (Persoz). Aluminium chloride also combines with phosphorus pentachloride, phosphorus oxychloride, the chlorides of silver, selenium, and tellurium, as well as with other metallic chlorides. It is largely employed for the synthesis of organic compounds.

Sodium Aluminium Chloride, $AlCl_3$,NaCl.—The preparation of this compound on the large scale has already been described. It is obtained as a colourless crystalline mass which melts at 185° (Bunsen) and volatilises at a red-heat. It readily absorbs water, but in the compact state it is less hygroscopic than aluminium chloride, and for this reason it was used instead of the latter compound in the preparation of aluminium.

Aluminium Bromide, $AlBr_3$.—When aluminium and bromine are brought together they combine with evolution of heat, forming the above compound. It is obtained by passing the vapour of bromine over a heated mixture of alumina and carbon. It is a colourless crystalline body which melts at about 90°, boils at a temperature between 265° and 270° and sublimes in crystalline scales. The specific gravity of the solid is 2·54. In other

[1] Seubert and Pollard, *Ber.* 1891, **24**, 2575.
[2] *Zeit. phys. Chem.* 1887, **1**, 459; 1889, **4**, 206.
[3] Dennis, *Zeit. Anorg. Chem.* 1895, **9**, 339.

respects it is analogous to the chloride, and forms the hydrate $AlBr_3 + 6H_2O$, which is also obtained by dissolving aluminium hydroxide in hydrobromic acid and carefully evaporating the solution.

Aluminium Iodide, AlI_3, is formed when the metal and iodine are heated together in closed tubes. It is deposited in colourless crystals which melt at 185° (Weber) and boil at a temperature of 360°. Its specific gravity is 2·63. The vapour is combustible, giving rise to an explosive mixture when diluted with air. It is soluble in water, alcohol, and carbon bisulphide, and forms with the first of these solvents a crystalline compound, $AlI_3 + 6H_2O$. Aluminium iodide has been employed for the purpose of converting organic chlorine compounds into iodides. Thus carbon tetra-chloride yields the corresponding tetra-iodide when heated with aluminium iodide (Gustavson):

$$4AlI_3 + 3CCl_4 = 4AlCl_3 + 3CI_4.$$

Aluminium and Sulphur.

282 *Aluminium Sulphide*, Al_2S_3.—Aluminium combines with sulphur at a red-heat to produce this compound [1] which is a yellow fusible mass. It is also formed when sulphur is added to a strongly heated mixture of alumina and charcoal [2] and when the vapour of carbon bisulphide is passed over strongly heated alumina.

It is decomposed by water with formation of sulphuretted hydrogen and aluminium hydroxide.

Aluminium Sulphate, $Al_2(SO_4)_3$, is obtained by dissolving the hydroxide in dilute sulphuric acid. It crystallises with difficulty, forming pearly six-sided monosymmetric tablets containing eighteen molecules of water. It possesses a sweet astringent taste, dissolves in two parts of cold water, but scarcely at all in alcohol (Berzelius). The hydrated salt, $Al_2(SO_4)_3 + 18H_2O$, is found as the mineral keramohalite in the neighbourhood of active volcanoes, and in alum-shale. It melts on heating in its water of crystallisation, and then swells up, the anhydrous compound being left behind as a porous mass, dissolving only slowly again in water. At a red-heat it is decomposed, leaving a residue of pure alumina. The

[1] Knapp and Ebell, *Dingl. Polyt. Journ.*, 1878, **229**, 69, 173.
[2] Bucherer, *Zeit. Ang. Chem.* 1892, 483.

concentrated solution of this salt is a useful reagent for potassium salts, as potassium alum, $Al_2K_2(SO_4)_4 + 24H_2O$, is precipitated as a crystalline powder, which is almost completely insoluble in an excess of aluminium sulphate.[1]

Aluminium sulphate is prepared on the large scale, and is known in commerce under the name of concentrated alum or sulphate of alumina. For this preparation china-clay, as free as possible from iron, is employed. This is roasted in a reverberatory furnace, by which any iron which may be present is rendered insoluble, whilst the silicate of alumina becomes more soluble in sulphuric acid. It is then heated in leaden boilers with sulphuric acid of specific gravity 1·45, and the solution allowed to deposit the silica, and any undecomposed alumina. The clear liquid is then evaporated down until a small portion on cooling is found to solidify. After cooling, the soft mass is cut into square blocks, and thus brought into the market. This material is employed by the dryer as a mordant, and also for the purpose of weighting paper and for the treat- of sewage.

An impure product, known under the name of *alum-cake*, also used largely by paper-makers, is obtained by heating a white china-clay or bauxite with sulphuric acid. The whole mass then becomes solid. It consists of about 12–15 per cent. of soluble alumina as sulphate, together with silica and undecomposed aluminate.

For many purposes a sulphate perfectly free from iron is needed. This is prepared by dissolving the pure hydroxide in sulphuric acid, or by treating a solution of the crude sulphate with pyrolusite (Spence) or calcium ferrocyanide solution (Kynaston).

According to Berzelius a series of basic sulphates of aluminium exists. These are probably mixtures. One of them occurs in clay deposits as the mineral aluminite or websterite. It forms an earthy mass, having the composition $Al_2(SO_4)(OH)_4 + 7H_2O$. The same salt is formed when aluminium sulphate is precipitated with a quantity of ammonia insufficient to throw the whole of the alumina down. When a concentrated solution of aluminium sulphate is boiled with the freshly precipitated hydroxide a thick solution is formed, and this, on standing for some months, deposits a crust of small needle-shaped crystals of a salt having the composition $Al_2(SO_4)_2(OH)_2 + 2Al_2(SO_4)(OH)_4 + 25H_2O$ (Rammelsberg).

[1] Wurtz, *Dict.* i. 174.

The Alums.

283 Aluminium sulphate forms with the sulphates of the alkali-metals double salts, which crystallise in regular octohedra, of which the potassium double salt, $Al_2(SO_4)_3 + K_2SO_4 + 24H_2O$, has long been known under the name of *alum*. This name is, however, now used to designate a whole group of bodies. A number of substances with an astringent taste were known to the Greeks (*στυπτηρία*), and the Romans (alumen), and among these the naturally occurring aluminium sulphate and alum seem to have been included. We also find the name occurring in the writings of the Latin Geber, who speaks of an ice-alum, which is obtained from Roccha, and which he was able to purify by re-crystallisation. The alchemists of the West described this salt as *alumen de rocca*, in order to distinguish it from the vitriols, and this name was afterwards erroneously translated by the French chemists, who termed pure alum *alun de roche*.

In the thirteenth century an alum factory, erected by Italians, existed near Smyrna. They obtained their alum by roasting alum-rock, lixiviating the product, and crystallising. In the fifteenth century the Genoese erected alum works on the island of Ischia, and at the same time the celebrated works at Tolfa, in the Papal States, were established. The so-called Roman alum, which was there prepared, was, up to recent times, considered to be the best, and the manufacture has been resuscitated, 10,000 tons of alum being made annually at Tolfa by a French company. The material from which the alum is manufactured in various places in Italy, as well as in Hungary, is the alum-rock, the chief constituent of which is the mineral alunite or alum-stone, which is itself a double compound of potassium sulphate and basic aluminium sulphate, possessing the formula $K_2SO_4 + 3Al_2(SO_4)(OH)_4$. The rock is a product of the action of steam and sulphur dioxide on trachyte, and consists chiefly of a mixture of quartz and alum-stone. This is mixed with fuel in heaps, or in a furnace similar to a lime-kiln, and the roasted mass exposed for some weeks to the air. It then falls to a soft material, which is lixiviated with hot water, and the clear liquid, on standing, is concentrated in copper pans, and allowed to crystallise in wooden vessels. The crystals have a slightly orange-red colour, a very characteristic property of

Roman alum, due to the presence of very finely divided ferric oxide, which is mechanically mixed in the mass. On crystallising the alum from hot water this is left behind in the form of a reddish deposit.

Another method for preparing alum has long been known, and is described by Agricola and Libavius. For this purpose shale is employed. This chiefly occurs in the Silurian and Devonian formations, and contains finely divided iron pyrites distributed through a mass of bituminous shale. The shale is heaped together, and is either allowed to decompose slowly by exposure to the air, or it is roasted. In either case the pyrites is oxidised with formation of ferrous sulphate and free sulphuric acid, both of which act upon the clay, producing aluminium sulphate, which is then dissolved out with water. It has long been known that the ley thus obtained does not crystallise until an alkali has been added to it. Both Agricola and Libavius state that it is customary to add decomposed urine to the ley, in order, as the latter author remarks, to separate out the vitriol which is contained in solution. The alum thus prepared must have been chiefly ammonia-alum. This conclusion is corroborated by Kunkel's remark, for we find that he states distinctly in his *Laboratorium Chymicum* that alum contains the volatile alkali. Instead of urine, potash was soon used, and Hoffmann, in 1722, explained why an alkali was added, and this explanation, namely, that the crude ley was unable to crystallise because it was too acid, and also because it contained a sulphurous impurity which had to be removed by the addition of alkali, was the one which was accepted as correct until the end of the last century. At that time, and even up to a later date, it was not generally admitted that an alkali formed an essential constituent of the alum. Moreover, alum was often prepared without the addition of such an alkali, for in those days the existence of a potassium compound in a mineral such as alunite was not known. Bergman and Scheele, who were well aware that alum contained potash, considered it to be an impurity. Marggraf then showed that pure alumina and sulphuric acid only formed an alum when an alkali was added, and hence Lavoisier concluded that two bases were contained in alum, viz., the alumina and the fixed alkali. These views were, however, not generally accepted until 1797, when Chaptal and Vauquelin showed that potash was an essential constituent of alum: the latter chemist moreover proved that this fixed alkali could be replaced by ammonia, and

asserted that when aluminous minerals yielded an alum on treatment with sulphuric acid it was a proof that these minerals contained potash.

The crude ley from the lixiviation of the burnt shale consists essentially of the sulphates of aluminium and iron. The longer the shale remains heaped up, and the longer the ley stands before it is further worked up, the smaller is the quantity of ferrous sulphate (green vitriol) which it contains, inasmuch as this salt is gradually converted by the oxygen of the air into ferric sulphate, which does not crystallise out with the alum. The solution is then evaporated down in order that the iron salt may be deposited, and the solution ultimately obtained, which has a specific gravity of 1·4, contains aluminium sulphate, with a small quantity of ferric sulphate. In order to obtain alum from this solution a potassium salt is added, and as the double salt formed is sparingly soluble, it separates out at once from the concentrated solution. Either potassium sulphate or chloride may be employed for this purpose: the first of course at once yields the alum together with ferrous potassium sulphate, which remains in the mother-liquor, a considerable quantity of potassium being thus lost. If potassium chloride be employed the alum is also at once precipitated; but aluminium chloride is found in solution. If, however, ferric sulphate be present, potassium sulphate is formed, and the readily soluble ferric chloride. Hence it is most economical to employ a mixture of the two potassium salts in different proportions, to be determined according to the composition of the ley. The crude potassium chloride from Stassfurt is now usually employed as the source of the potash. This substance is dissolved in a small quantity of hot water, and the solution added to the crude ley, and alum-meal is then obtained by well stirring the mixture until it is cold. The small crystals of which the meal consists are washed with a small quantity of cold water, the first wash-water being allowed to run into the boiling-down pans, and the last wash-water being employed for washing the crude alum. The purified meal is then dissolved in boiling water or by means of a current of steam, and the solution brought into large crystallising vats built of movable staves, bound together with iron hoops. In these the alum is deposited in the large crystals in which it is usually found in commerce.

Until recent years the chief quantity of alum made in England has been ammonia-alum, prepared according to Spence's

method. In this process the black bituminous shale lying above the coal-measures is employed as the source of alumina. This is made into heaps about 1·5m. in height and slowly roasted. The mass, which when roasted has a light red colour and is brittle, is then brought into large covered pans, and heated with sulphuric acid diluted with washings obtained in the final stages of the process, by means of steam coils placed in the pan, until the liquors contain only a small percentage of free acid. The impure solution of sulphate of alumina is then run into cooling tanks, on the way receiving a sufficient quantity of either ammonium or potassium sulphate to convert it into ammonium or potassium alum as required. It is then diluted with liquors from a later stage in the process and stirred until cold to obtain small crystals of alum meal, the the liquor run off, and the mealy alum washed with liquors and a small quantity of water. This is then drained and brought into a funnel-shaped vessel, where steam is allowed to blow on it in such a manner that the whole of the steam is condensed and all the salt dissolved. In half an hour about four tons of alum-meal can thus be dissolved. The solution is allowed to settle in lead-lined cisterns, and then brought into crystallising vats and allowed to remain in them for a week. The staves are then knocked away, and a cylindrical block of alum remains, which is allowed to stand another week. A hole is afterwards drilled into the bottom of the block, the mother-liquor allowed to run out, and the mass broken up. Each vat yields three tons of large crystals, which frequently possess an amethystine tint resembling alum containing much iron, although it contains less than 0·001 per cent. of that metal. This colour is probably due to exceedingly minute quantities of iron and chromium and not to organic matter as has been usually supposed.

Since the introduction of cheap potassium chloride from Stassfurt, ammonia-alum is no longer so largely made in England, potassium sulphate being manufactured by the action of sulphuric acid upon the natural potassium chloride in an ordinary salt-cake furnace, and employed instead of ammonium sulphate.

Shale is no longer used in many works as a source of alum, bauxite being employed and submitted to a similar treatment.

284 *Potassium-Alum*, $Al_2(SO_4)_3 + K_2SO_4 + 24H_2O$, is found

in nature in feathery or mealy crusts or masses, as an efflorescence on alum-shale, and in volcanic districts, where it is formed by the action of sulphur dioxide and oxygen on trachyte and lava. In some places, as in the districts near Naples and in Sicily, alum is produced in sufficient quantity to render its manufacture possible, and a very pure alum is obtained from this source. Potash-alum has a specific gravity of 1·724 (Kopp); it crystallises in transparent regular octohedra, which often exhibit the cube and dodecahedron faces; its solution possesses a sweet astringent taste, and has an acid reaction. 100 parts of water dissolve (Poggiale):

At	0°	10°	20°	30°	40°	50°	
$K_2Al_2(SO_4)_4+24H_2O$	3·9	9·5	15·1	22·0	30·9	44·1	parts.

At	60°	70°	80°	90°	100°	
$K_2Al_2(SO_4)_4+24H_2O$	66·6	90·7	134·5	209·3	357·5	parts.

It is insoluble in alcohol. On exposure to the air the surface becomes opaque and white. This is not, however, due to a loss of water, but is caused by the absorption of ammonia and the formation of a basic sulphate. When a crystal of alum is placed over sulphuric acid or heated to 61°, it loses 18 molecules of water (Graham); at 92° it melts in its own water of crystallisation, and loses the whole of its water slowly at 100°, and quickly at a higher temperature with formation of what is known as burnt alum. This forms a porous mass, which dissolves slowly but completely in water. When alumina is fused with hydrogen potassium sulphate, an anhydrous alum is obtained which crystallises in small six-sided crystals, which remain behind when the fused mass is treated with hot water.

Neutral and Basic Alums.—If an alkali be slowly added to an alum solution, a precipitate is thrown down which disappears on stirring, but after a further addition of the alkali it remains unaltered. The solution in which the precipitate just redissolves has a neutral reaction, and is termed in commerce neutral alum; it is employed in dyeing, as it readily gives up alumina to the colouring matter, and is free from iron, inasmuch as the alkali decomposes any iron sulphate which the liquid may contain. If this solution be allowed to evaporate at the ordinary temperature, a crystalline crust is deposited which contains the basic salt $Al_2(SO_4)_3 + 2Al(OH)_3$, together with

potassium sulphate. If the solution be heated above 40°, common alum is formed, and a precipitate of $K_2SO_4 + Al_2SO_4(OH)_4$ is thrown down, this latter substance being identical in composition with alunite from Tolfa. When a solution of basic alum is heated in sealed tubes to 230°, this compound is also obtained in crystals (Mitscherlich). Solutions which contain a small quantity of basic alum yield, on spontaneous evaporation, cubical crystals. These were first observed by Sieffert in 1772, and obtained by him by boiling alum with milk of lime. This so-called cubic-alum has the same composition as common octohedral alum, and on heating the solution, to which a small quantity of alkali has been added, to a temperature above 100°, ordinary octohedral alum separates out. Roman alum obtained from alunite often occurs in commerce in cubical crystals.

Rubidium and cæsium also form alums which are very difficultly soluble, and hence are employed, as has already been described, for the separation of these metals from potassium.

Ammonium-Alum, $Al_2(SO_4)_3 + (NH_4)_2SO_4 + 24H_2O$.—This salt is very similar to potassium-alum. It has a specific gravity of 1·626, loses water on heating, and, on ignition, leaves a residue of pure alumina. One hundred parts of water dissolve (Poggiale):

At	0°	10°	20°	30°	40°	
$Al_2(NH_4)_2(SO_4)_4 + 24H_2O$	5·2	9·1	13·6	19·3	27·3	parts.

At	50°	60°	70°	80°	90°	100°
$Al_2(NH_4)_2(SO_4) + 24H_2O$	36·5	51·5	72·0	103·0	187·8	422·0

Commercial alum frequently contains both potassium and ammonium in varying proportions.

A hydroxylamine alum is also known.

Sodium-Alum, $Al_2(SO_4)_3 + Na_2SO_4 + 24H_2O$.—It was formerly believed that aluminium sulphate did not form an alum with sodium sulphate, but this salt was prepared in the year 1816 by Zellner. Sodium alum is much more readily soluble in water than the other alums. Its specific gravity is 1·6. It effloresces in the air, and loses the whole of its water at a temperature of from 40° to 50°, leaving an easily soluble residue. It is not manufactured on the large scale, as on account of its solubility it is difficult to prepare in the pure state.

Silver Alum, $Al_2(SO_4)_3 + Ag_2SO_4 + 24H_2O$.—The isomorphism of many silver salts with the corresponding salts of sodium

connects this metal closely with those of the alkalis, and silver likewise forms an alum. This is obtained by heating a mixture of silver sulphate and aluminium sulphate, together with some water, in sealed tubes, until the silver sulphate is dissolved. On cooling, octohedral crystals are deposited. These are, however, decomposed into their constituents by water.[1]

Besides the above-mentioned alums, a number of other alums are known, in which the aluminium is replaced by isomorphous metals, such as iron, manganese, and chromium. A peculiar nomenclature has arisen in the description of these compounds. If none of the isomorphous metals replace aluminium, as in the above-mentioned alums, each is an aluminium-alum. The names, iron-alum, chromium-alum, and manganese-alum, on the other hand, are used, as a rule, to designate the potassium double sulphates of these metals. If potassium be replaced by other metals, then the names of both metals must be mentioned, as, for instance, ammonium-chrome-alum, and so forth.

Selenic acid also forms a series of alums, having the general formula, $M_2^{III}(SeO_4)_3 + M_2^{I}SO_4 + 24H_2O$.

Aluminium and Nitrogen and Phosphorus.

285 *Aluminium Nitride*, $(AlN)_x$, is formed in small yellow crystals when aluminium is strongly heated in nitrogen.[2] It is rapidly decomposed by water.

Aluminium Nitrate, $Al(NO_3)_3$, is obtained by dissolving the hydroxide in nitric acid, and evaporating the solution with occasional addition of nitric acid. On cooling, the salt $Al(NO_3)_3 + 8H_2O$ separates out in very deliquescent prismatic needles. This salt decomposes at 150°, leaving a residue of pure alumina (Deville), and this reaction may be employed for the separation of aluminium from calcium and magnesium, metals whose nitrates do not decompose at so low a temperature. The solution of the normal nitrate is obtained by exactly precipitating a solution of lead nitrate with aluminium sulphate. This solution is used as a mordant in calico-printing with alizarin colours.

Phosphates of Aluminium.—Normal *aluminium ortho-phosphate*, $AlPO_4$ is obtained as a gelatinous precipitate by adding

[1] Church and Northcote, *Chem. News*, 1864, **9**, 155.

[2] Briegleb and Geuther, *Journ. Chem.. Soc.* 1876, i. 349.

a neutral solution of an aluminium salt to a solution of sodium phosphate. It is soluble in alkalis and mineral acids, but not in ammonia. If an acid solution of the salt be precipitated with ammonia, a basic salt $3AlPO_4 + 5Al(OH)_3$, is thrown down; this, combined with nine molecules of water, forms the crystalline mineral wavellite. In addition to this, many other basic and double phosphates of aluminium occur in the mineral kingdom, of which the mineral turquoise or calaite, occurring in Persia and valued as a gem, is one of the most important. This is coloured of a greenish or bluish colour by copper, and is the basic salt $AlPO_4 + Al(OH)_3 + H_2O$. Most of the turquoise, not artificial, used in jewellery in former centuries as well as at the present time, and described in early works on mineralogy, is bone-turquoise or odontolite, a fossil bone or tooth coloured by phosphate of iron.

Aluminium and Silicon and Boron.

286 The compounds of aluminium and boron have been described in vol. i. p. 643.

It has already been stated that the various silicates of aluminium occur in combination with other silicates to form the chief constituents of the solid crust of the earth. The number of these compounds is extremely large, and only those can be mentioned in this work which possess a general interest.

Topaz, $Al_2SiO_4F_2$, occurs in granite, gneiss, and mica-schist in the form of rhombic prisms, which are transparent and usually colourless, or of a light- or dark-yellow colour. The finest topaz occurs in the Urals, Siberia, and Brazil. The common forms are not infrequently employed for the manufacture of polishing powder instead of emery.

Beryl, $Be_3Al_2(SiO_3)_6$.—The transparent green variety which owes its colour to chromium oxide is usually termed emerald. This mineral has already been described under beryllium.

Noble Garnet $(Mg,Fe)_3Al_2Si_3O_{12}$.—This, like the other members of the group of garnets, crystallises in the regular system, the dodecahedron being the most prominent form. The crystals are transparent, and are coloured, according to the quantity of iron which they contain, from a pale yellow up to a dark red tint.

Ultramarine.

287 A double silicate of aluminium and sodium containing sulphur, known as *lapis lazuli*, has long been valued for its splendid blue colour. Its constitution is, however, as yet unknown. It crystallises in dodecahedra, but usually occurs in the massive condition, and is found in Central Asia, Siberia, Persia, China, &c. It is largely used for making vases and for inlaying ornamental furniture, and the powdered lapis lazuli forms a valuable paint termed ultramarine. This substance is, however, now artificially prepared on the large scale.

Tessaert observed in 1814 the formation of a blue colour in one of his black-ash furnaces at the celebrated glass-works of Saint Gobain, and Vauquelin showed that this colour was identical with lapis lazuli. In 1824 a prize was offered in France for the discovery of a practical method of manufacturing this colour, and this problem was successfully solved in the year 1828 simultaneously by Guimet [1] and Christian Gmelin, the latter of whom published the process in the year 1828.[2]

Since this date the ultramarine industry has largely increased. The chief quantity of the substance is manufactured in Germany, and the total production now amounts to about 10,000 tons per annum. In the year 1829 the price of artificial ultramarine was £12 per lb., whereas now it is sold at less than 30s. per cwt. Different varieties of ultramarine occur in commerce; these, however, can be divided into two classes.

Ultramarine poor in silica is obtained by heating a mixture of soft clay with Glauber's salt, charcoal, soda, and sulphur in crucibles placed in a furnace. Instead of charcoal, tar or resin is sometimes employed. In this way a colourless compound is first produced, termed white ultramarine. This, however, soon becomes of a green colour. The green ultramarine thus obtained, which is also used as a colour, is then mixed with sulphur and heated. The sulphur takes fire and is allowed to burn in the air, when the product becomes of a fine blue colour. *Ultramarine rich in silica* is generally obtained by heating a pure clay with finely ground white-sand, sulphur, and resin or charcoal in a muffle-furnace, when a blue product is at once obtained which, according to the quantity of silica originally

[1] *Ann. Chim. Phys.* 1831, **46**, 431.
[2] *Quart. Journ. Science*, **2**, 216.

added, retains more or less of a red tinge. The different kinds of both green and blue ultramarine are then finely ground and washed with water, and thus the several marketable varieties are obtained. A violet and a red variety of ultramarine have also been prepared. The following table gives the composition of some different ultramarines :—

		Blue.	
	Green.	Poor in Silica.	Rich in Silica.
SiO_2	38·52	37·90	40·77
Al_2O_3	28·94	29·30	23·74
Na_2O	23·68	22·60	18·54
S	8·30	7·86	13·58
Earthy residue	1·94	2·36	3·61
	100·38	100·02	100·24

It has already been stated that the chemical constitution of ultramarine is, as yet, unknown.[1] The sulphur present is, however, contained in two conditions. Acids readily decompose all the different kinds of ultramarine, gelatinous silica and finely divided sulphur being deposited and sulphuretted hydrogen evolved. According to Heumann, blue ultramarine most probably has the composition of a double compound of sodium aluminium silicate and sodium sulphide, $2Na_2Al_2Si_2O_8 + Na_2S_2$, and is intimately related to the minerals kaolin, $H_2Al_2Si_2O_8 + H_2O$, nepheline, $Na_2Al_2Si_2O_8$ and hauyn, $2Na_2Al_2Si_2O_8 + Na_2SO_4$, the last of which is of a blue colour. The ultramarine which is poor in silica is decolorised by the action of a cold solution of alum, whilst the ultramarines rich in silica withstand the action of this salt, and the more completely the more silica they contain. Hence these latter varieties are employed in cases in which the colouring matter comes in contact with aluminium salts, as for instance in the blueing of paper and in calico-printing. The different kinds of ultramarine are very largely employed in the arts, for water-colours, as an oil-paint, and for paper-staining.

Silver-Ultramarine.—When blue ultramarine is heated with a solution of silver nitrate, the sodium is replaced by silver, and a yellow powder is thus obtained which under the microscope is seen in the form of dark lemon-yellow transparent particles. It is easily decomposed by acids with separation of silica, one third

[1] See article "Ultramine," *Thorpe's Dict. of Applied Chem.* and Dammer, *Handbuch*, **3**, 193, where references are given to the literature of the subject.

of the silver being precipitated as silver sulphide, but without evolution of sulphuretted hydrogen. If silver ultramarine be heated with a solution of potassium chloride the silver is replaced by potassium, and in this way blue potassium ultramarine is obtained, a substance which has hitherto not been prepared directly (Heumann). A bright blue lithium ultramarine has also been prepared in a similar manner. Organic derivatives of ultramarine, such as ethyl ultramarine, have also been obtained from the silver compound by the action of the alcoholic iodides. Ultramarines containing selenium and tellurium in place of sulphur have moreover been prepared.

Detection and Estimation of Aluminium.

288 Aluminium compounds do not impart any colour to the non-luminous gas-flame. The spark-spectrum of aluminium has been mapped by Thalén, Kirchhoff, and Lecoq de Boisbaudran, and its spectrum in the electric arc by Liveing and Dewar and by Kayser and Runge. The last named investigators found that the visible portion of the spectrum did not contain a single line. The aluminium bands in the ultra-violet, however, are extremely characteristic. These are contained in the invisible and highly refrangible portions of the spectrum which are only seen when the rays are allowed to fall on a fluorescent substance.[1] Alumina also shows a characteristic spectrum even in the arc.

Aluminium occurs almost always combined with oxygen. Most of these compounds are insoluble in water; many of them, however, are decomposed by hydrochloric acid, the alumina entering into solution. Those compounds which withstand the action of acids are decomposed by fusion with sodium carbonate and treatment of the fused mass with hydrochloric acid. Corundum, spinelle, and some other minerals are not, however, decomposed in this way: the best method for obtaining the aluminium in solution is to fuse these substances with hydrogen potassium sulphate.

Aluminium can readily be separated from all other metals. It is not precipitated from its acid solutions by sulphuretted hydrogen, whereas it is completely thrown down as the hydroxide by

[1] Stokes, "On the Long Spectrum of the Electric Arc," *Phil. Trans.* 1862, 599.

ammonia and sulphide of ammonium, and thus can be readily separated from the metals of the alkalis and alkaline earths. It is distinguished from most of the metals precipitable by sulphide of ammonium, inasmuch as its hydroxide is soluble in caustic alkalis. This property it possesses in common with the hydroxides of zinc, chromium, and beryllium. The first of these metals is precipitated from the alkaline solution by sulphuretted hydrogen, and chromium hydroxide is only soluble in the cold, and is precipitated on boiling. If to the solution from which the zinc and chromium have thus been separated, hydrochloric acid and then ammonia be added, the aluminium is precipitated. This precipitate may, however, still contain beryllium hydroxide, which must be dissolved by digesting it with ammonium carbonate (p. 468). When the oxide is strongly heated with a salt of cobalt, a bright blue mass is obtained.

For quantitative estimation, aluminium is precipitated as hydroxide, and this converted into the oxide by strong ignition.

The atomic weight of aluminium was first determined by Berzelius in 1812, who found that 100 parts of the anhydrous sulphate yielded 29·934 parts of pure alumina, according to which the atomic weight is 27·1.[1] Tissier[2] found the number 27 by the conversion of the metal into the nitrate and then into the oxide, and Dumas[3] 27·3 by the analysis of the chloride. The most reliable determinations are due to Mallet,[4] who employed three distinct methods: the ignition of ammonium alum, which gave the number 26·89; the analysis of the bromide, from which the atomic weight appeared to be 26·91; and finally, the direct determination of the equivalent to hydrogen. This last set of experiments was carried out by dissolving pure aluminium in concentrated aqueous soda, and collecting and measuring the dry hydrogen produced. He thus found that 3·352 grm. of aluminium yielded 4161·6 c.c. at the normal temperature and pressure (in 45° north latitude). According to this, the equivalent of aluminium is 8·969, and the atomic weight 26·91. In a second series of less reliable experiments the hydrogen was burned and the water weighed. The mean atomic weight of aluminium may therefore be taken as 26·91.

[1] *Pogg. Ann.* 1812, **8**, 187.
[2] *Compt. Rend.* 1858, **46**, 1105.
[3] *Ann. Chim. Phys.* 1859 [3], **55**, 151.
[4] *Phil. Trans.* 1880, 1003.

GLASS, PORCELAIN, AND EARTHENWARE.

289 The naturally-occurring silicates are almost all of them crystalline, and are thereby distinguished from those produced artificially, which are usually amorphous. Amongst these latter may be classed glass, porcelain, and the various kinds of pottery.

GLASS.

The manufacture of glass appears to have been discovered by the Egyptians, although the ancients themselves attributed the discovery of glass-making to the Phœnicians. Glass vessels of various sizes, both colourless and coloured, have been found in Egyptian tombs which belong to an age prior to that in which the Phœnicians occupied themselves with glass-making. Indeed the latter nation appear rather to have been engaged in exporting the glass made in Egypt, and especially at Thebes, into different parts of the ancient world, than to have established any original manufacture of their own. In the tombs of Beni Hassan near Thebes, which were built more than 2000 years B.C., we find paintings representing Egyptians carrying on the processes of glass-blowing. From these, as well as from the glass vessels which are found in the tombs, it appears that the Egyptians were not only acquainted with the art of glass-making and of working in glass, but likewise with that of cutting and colouring glass by which they imitated precious stones. Thus an urn has been found made of white glass and ornamented with patterns in white and in light- and dark-blue glass showing Thoutmosis' ring, who reigned in the 17th century B.C. Specimens illustrating all the stages of the process of glass-making, and dating from about 1400 B.C., have been found at Tell el Amarna.[1]

Aristophanes is the first Greek author who mentions glass (ὕᾰλος), and in his *Clouds* he refers to a glass lens which was used as a burning-glass. Amongst Latin authors, Cicero is the first to mention Egyptian glass, and we find that at the time

[1] For further information see Sir Gardner Wilkinson, *The Manners and Customs of the Ancient Egyptians*, vol. iii. p. 88, edit. 1837; and *Tell el Amarna* by W. M. F. Petrie (London, 1894).

of Augustus the Egyptian glass was highly valued in Rome, so much so that when this emperor subdued Egypt (29 B.C.), a portion of the tribute was ordered to be paid in glass; this material afterwards being so highly valued by the Romans that Aurelius levied an import duty upon it.

Glass-works were established in Italy, France, and Spain at an early date. These glass-houses, however, only manufactured common objects for every-day use, and it was not until after the introduction of Egyptian workmen to Rome that artistic glass-ware was made in Europe. This took place during the reign of Tiberius, and the art made such rapid progress that in the time of Nero, Roman glass rivalled in every respect the original Egyptian manufacture. According to Pliny, Egyptian soda and sand were employed in the manufacture of glass, and he remarks that in India rock-crystal was used for this purpose, and that in his time the material which was most highly valued for making glass was that which approached most nearly to this mineral. This is readily understood when we remember that most of the materials used for the manufacture of glass contain metallic oxides, which produce a colouring effect upon the mass, so that it is in fact easier to produce coloured than colourless glass. And even in those early days we find that manganese was employed as a decolorising agent. Pliny moreover specially mentions the preparation of coloured glass, whilst analyses of antique glass show that the materials employed to produce the colours in those days were identical with those which are at present in use.

After the fall of the Western Empire the glass manufacture followed Constantine to Byzantium, and for five centuries the Eastern capital became a renowned seat of the glass manufacture. On the decay of the Empire of the East, the glass-makers wandered to various parts of Europe, many being attracted to the Venetian Republic. Here glass-making greatly flourished. As a protection against fire, as it is said, the manufacture of glass was removed in the year 1289 from the city of Venice to the adjacent Island of Murano, and here during the 16th and 17th centuries the Venetian glass-manufacture attained its highest development, the elaborate productions of Venetian art becoming famous throughout the civilised world. No less than 8,000 men were, it is stated, employed at that time in the manufacture, and so important did this branch of Venetian trade become, that strict laws were promulgated to prevent the

secrets of glass-making from becoming known to foreign workmen, the supervision of the glass-houses being confided to the chief of the Council of Ten. The Venetian glass-industry received, however, a check in the 17th century, from which it has only in recent years recovered.

290 In the early Middle Ages an independent manufacture of glass arose in Germany, and glass-painting is entirely of German origin; the manufacture of glass mirrors appears also to be a German invention. At first the glass was coated with a plate of metal, and it was not until the 15th century that the present process was introduced. In addition to table-glass and window-glass, artificial gems, glass rings, and other objects of art were manufactured in Germany. Agricola in his treatise *De re Metallica*, published in the year 1530, gives the first drawing of the interior construction of a glass-furnace, and in this work as well as in Mathesius' *Sarepta or Bergpostill* (1564), we find explicit and interesting directions concerning the manufacture of glass as carried on in Venice, Germany, and Bohemia. In the last-named country the glass-industry began to flourish in the 16th century, the purity of the materials occurring there enabling manufacturers to produce the colourless glass for which the Bohemian glass-houses have long been famous and in which they still excel. When the Venetian glass-manufacture fell into decay, Bohemian glass replaced Venetian, but in time the Bohemian manufacture again suffered a relapse, owing to the heavy import duties which were levied upon glass-wares as well as to the fact that other governments held out inducements to the Bohemian workmen to settle in foreign countries; like the Venetian manufacture, it is only in recent years that the Bohemian glass-industry has recovered its original position.

In the meantime many of the German princes patronised the glassmakers, and each became celebrated for some peculiar manufacture. Thus a glass-house at Potsdam was well known for its manufacture of ruby glass. This glass-house was established under the direction of Joh. Kunkel, and in 1685 he published the first edition of his *Ars Vitraria Experimentalis*, in which he gave a translation of the collection of receipts published at Florence by Antonius Neri in 1612, and added to them remarks of his own and those of E. Merret.

Glass-works were also set up in France at an early date, but it was not until the 18th century, when workmen were introduced from Germany, that a pure kind of French glass-ware

was made. Plate- or mirror-glass was first prepared in England, but the method of manufacture was greatly improved by De Nehou, who in 1688 erected a glass-works at Paris. This was afterwards removed to St. Gobain, where it soon became and still remains the most important plate-glass works in the world.

The first manufacture of glass which we hear of in England is that of window-glass established in the 15th century. The product cannot, however, have been very good, for in an old deed made in 1439 by the Countess of Warwick and a glazier of Westminster named Prudde, it is distinctly stipulated that no English window-glass is to be used. In the reign of Elizabeth, French artists were brought to London, and these carried on their trade of making window-glass at Crutched Friars in 1557, whilst flint-glass was first manufactured at a glass-house at Savoy House in the Strand. Mirror-glass, used for looking-glasses, coach-windows and similar purposes, was manufactured at Lambeth by Venetian workmen brought over in 1670 by the Duke of Buckingham. The first large plate-glass works were established in 1771 at St. Helens under the name of the Ravenshead or the British Plate-Glass Company, and this company continues to flourish up to the present time.

The glass-industry was introduced into Russia in the 17th and 18th centuries by German and Bohemian workmen; and in the United States the same manufacture appears to have been established by Robert Hewes, a citizen of Boston, who erected a glass-house in the forest which existed in New Hampshire. The manufacture of Mr. Hewes does not seem to have been successful, and in 1800 another attempt was made to establish a glass-house at Boston, which also failed, until a German of the name of Lint took charge of the works in 1803, and the State of Massachusetts agreed to pay a bounty on all glass manufactured by him.

291 *Composition of Glass.*—Glass is an amorphous mixture of various silicates, especially of those of the alkalis and alkaline earths, formed by the fusion of the ingredients. Glass differs from any of the simple silicates which compose it by being nearly insoluble in water and in acids, as well as by being non-crystalline; for whilst the silicates of the alkalis yield a non-crystalline mass on cooling from fusion, which is soluble in water, the silicates of the alkaline-earth metals, on the other

hand, yield, after fusion, a distinctly crystalline solid readily attacked by acids. At high temperatures glass fuses to a thin mobile liquid, and on cooling this passes through all gradations of viscosity until the solid state is reached. This property of glass to pass gradually from the liquid to the solid condition is one which is peculiarly characteristic of the substance, and it is this which caused Pliny to consider glass as the most plastic of substances.

Owing to the immense number of its applications to the purposes of every-day life, the manufacture of glass has greatly contributed to the progress of civilisation, whilst from a scientific point of view the value of glass can scarcely be overrated, as the sciences of chemistry and physics could scarcely exist were it not for this most useful material.

292 The several kinds of glass may be roughly divided according to their composition into four chief varieties:

I. *Bohemian Glass.*—This is a silicate of potash and lime. It is very difficultly fusible, and is not easily acted upon by chemical reagents.

II. *Window- or Crown-Glass.*—This is a silicate of soda and lime. It is more fusible but harder than the preceding, and possesses the faint blue colour characteristic of soda glass; it is more readily acted upon by acids than Bohemian glass.

III. *Bottle-Glass or Common Green Glass* is a silicate of soda and lime, together with alumina and oxide of iron, and it is to this latter oxide, present as impurity in the cheap materials employed, that the mass owes its green colour. The alkaline silicates are contained in bottle-glass in smaller quantity than in the other varieties of glass, and the colour varies from a darker to a lighter green or brown according to the care with which the materials have been selected. It is harder and more infusible than soda-lime glass, but it is easily attacked by acids.

IV. *Flint-Glass or Crystal, and Strass.*—This glass is a potash-lead silicate. It is characterised by its high specific gravity, bright lustre, and great refractive power. It is the most fusible variety of glass, and is easily attacked by chemical reagents. Crystal is a pure flint-glass used for optical purposes. Strass is a flint-glass, named after the discoverer, very rich in lead, and possessing a very high refractive power; it forms the basis of the imitation gems and precious stones known as *paste.*

The following table shows the composition of samples of the different kinds of glass:—

Description of Glass.	SiO_2.	K_2O.	Na_2O.	CaO.	MgO.	PbO.	Al_2O_3.	Fe_2O_3.	*Analyst.*
I. Bohemian Glass—									
Old goblet	69·40	11·80	—	9·20	—	—	9·60		Dumas.
Drinking glass	71·70	12·70	2·50	10·30	—	—	0·90		Berthier.
Mirror glass	76·00	15·60	—	8·00	—	—	1·00		Péligot.
Combustion tube	73·13	11·49	3·07	10·43	0·26	—	0·89		Rowney.
II. Crown-, Window-, & Plate-Glass—									
Old Egyptian glass	72·30	—	20·83	5·17	—	—	1·19	0·59	Benrath.
Roman bottle	70·66	—	17·17	8·38	—	—	2·25	1·24	,,
German window-glass	71·56	—	12·97	13·27	—	—	1·29		,,
English window-glass	70·71	—	13·25	13·38	—	—	1·92		,,
French window-glass	71·90	—	13·10	13·60	—	—	1·40		Péligot.
German hollow glass	78·39	—	13·91	7·10	—	—	0·60		Benrath.
French hollow glass	72·00	—	17·00	6·50	—	—	4·50		Berthier.
English crown-glass	71·40	—	15·00	12·40	—	—	0·60		Cowper.
German crown-glass	73·11	—	13·00	13·24	—	—	0·83		Benrath.
Plate-glass from St. Gobain	73·00	—	11·50	15·50	—	—	—	—	Péligot.
English plate-glass	77·90	1·72	12·53	4·85	—	—	3·59		Mayer and Brazier.
German plate-glass	78·75	—	13·00	6·50	—	—	1·75		Benrath.
Venetian plate-glass	68·60	6·90	8·10	11·00	2·1	—	1·50		Berthier.
III. Bottle-Glass—									
German	65·57	2·72	4·86	20·42	—	—	3·34	2·81	Schuler.
French	59·60	3·20		18·00	7·00	—	6·80	4·40	Berthier.
IV. Flint-Glass—									
English flint-glass	51·40	9·40	—	—	—	37·40	2·00		Berthier.
French flint-glass	50·18	11·22	—	—	—	38·11	—	0·44	Benrath.
Heavy optical glass	44·30	11·75	—	—	—	43·05	0·50	0·12	Faraday.
Strass	38·10	7·90	—	—	—	53·00	1·00		Donault-Wieland.

293 The materials used in the glass manufacture are, in the first place, silica, which is contained in all forms of glass. This substance is added in the form of white sand, ignited flint, or quartz. For the common kinds of glass common sand is used. The second important ingredient is the alkali, and this is added in the form of purified potashes; whilst the alkali used for the better kinds of soda-glass is added in the form of refined soda-ash. For the commoner sorts of glass sodium sulphate, or salt-cake, is now largely employed instead of soda-ash; this being transformed into sodium silicate by the silica, in the presence of carbon, with evolution of sulphur dioxide.

The materials employed for the formation of the other constituent of glass, viz., calcium silicate, are, according to the kind of glass needed, calc-spar, marble, chalk, or common limestone. In the manufacture of lead-glass red-lead is employed, and for the common varieties white-lead or litharge is sometimes used.

The less iron is contained in the materials used, the whiter and less coloured will be the glass. It is, however, almost impossible to obtain materials perfectly free from iron oxide, and, in consequence of this, a substance is generally added for the purpose of oxidising the ferrous oxide to ferric oxide. The former oxide, even in small quantities, imparts to glass a deep-green tint, whereas the latter gives to the glass a light-yellow colour, and this is scarcely visible when the ferric oxide is present in small quantities. The decolorising substances added for this purpose likewise serve to oxidise the carbon which is frequently present in the mass, and which imparts to the glass a deep-yellow or brown tint. Manganese dioxide (pyrolusite), arsenic trioxide, and saltpetre are used as decolorising agents in the manufacture of lime-glass, whilst red-lead is employed for the same purpose in the manufacture of flint-glass. In former times manganese dioxide (pyrolusite) was exclusively used for this purpose. Indeed the Romans were acquainted with this property of manganese dioxide (see Manganese), and on account of its detergent qualities it was in later times called *sapo vitriariorum*, or glass-maker's soap. The decolorising action of manganese dioxide upon glass not only depends upon the fact that it oxidises the iron from ferrous to ferric oxide, but also that the manganese itself imparts to the glass a violet tint, and this being a colour complementary to the colour produced by the iron salt, assists in the decolorisation.

294 (1) *Bohemian Glass* is made from pure powdered quartz and purified potashes, and is distinguished by its colourless character, which approaches that of rock-crystal itself. In consequence of this property it has long been highly esteemed, and Bohemia is the seat of a wide-spread industry, which, however, has somewhat declined since the general introduction of flint-glass. Bohemian glass serves for the preparation of chemical apparatus, and especially of combustion-tubes, which withstand a high temperature without softening.

(2) *Window-, Crown-, or Plate-Glass.*—From the preceding table it is seen that the glass of ancient Egypt possesses a very similar constitution to that which is now largely manufactured for the above purposes, and the Egyptians appear to have employed for the manufacture the naturally occurring carbonate of soda, or trona, which is found in Upper Egypt. In Europe, and especially in France, kelp, or, at any rate, carbonate of soda obtained from kelp, was originally employed for glass-making; but this source of soda was replaced in England in the year 1831 by soda-ash, made by Leblanc's process. Laxmann in 1764 had already tried to replace the carbonate by the native sulphate occurring in the Siberian salt-lakes, and these experiments were continued in 1803 by Baader, who succeeded in replacing soda-ash by salt-cake in the manufacture of common glass; but it is only since 1856, when Pélouze found a simple method of obtaining the sulphate free from iron, that the latter has almost entirely superseded the more expensive soda-ash. The whole of the sulphur contained in the salt-cake is evolved as sulphur dioxide, and this escapes into the air, no practical process having, as yet, been suggested by which this gas can be condensed and utilised.

(3) *Common Bottle-Glass or Green Glass.*—Figures of glass-blowers plying their trade have been found in the Theban tombs of Beni Hassan, where the workmen are represented as using blow-pipes, and other tools similar to those which are now employed, whilst the bottles, and other products of the glass-blower's art (shown in the paintings) are not unlike similar objects of our own day. Bottles have also been discovered in the Theban tombs inscribed with Chinese characters. May not this fact point to a possible connection between Egypt and the still older monarchies of the far East? In vine-growing France the necessity for glass wine-bottles soon became felt, and a glass-bottle works was established so early as the year 1290 by

Leempoel, at Quiquengrogne, near La Chapelle, which is flourishing at the present day.

Bottle- or green glass is the commonest kind of glassware. The materials employed for its preparation are common coloured sand, the residual alkaline- and lime-salts from gas-works, soap-works, and alkali-works; common-salt, salt-cake, and ashes from fires of wood or charcoal; clay, basalt, and other rocks containing felspar.

The first essential of a wine-bottle is that it shall be strong, and that it shall not be attacked by the acids contained in wine. This last property depends upon the composition of the glass, for if it does not contain a sufficient quantity of silica, the glass is apt to be attacked by acids. The common, half-white blown-glass, stands, both in its composition and in its mode of preparation, between green bottle-glass and the pure white-blown glass, and the materials for its preparation must be free from iron. All the glass has, however, more or less of a green tint. In England common medicine bottles, as well as the large stoppered bottles, known as Winchester quarts, are tinted a light blue colour by the addition of oxide of cobalt.

(4) *Flint-Glass or Crystal.*—This glass contains lead oxide as its characteristic ingredient, and hence is frequently termed lead-glass. The name flint-glass was given to this product because burnt and ground flints were originally used as a source of silica. It is usually supposed that the manufacture of this glass was first carried on in England, and at the present day the article is a characteristic product of the English glass-house. It appears, however, that flint-glass was known to Neri, who describes it as by far the most beautiful glass, and in Kunkel's translation he says: "Lead-glass is not in use amongst our glass-makers on account of its great brittleness." At any rate lead-glass was made in England about the year 1635, and its manufacture was carried on by means of coal, which was first employed as fuel in the glass-houses in that year in place of charcoal. The carbonaceous smoke of the burning coal imparted to the ordinary glass a yellow colour, but this difficulty was overcome by the use of covered crucibles instead of the open ones formerly used (see Figs. 136 and 137). The drawback to the use of such crucibles was that they did not attain a sufficiently high temperature to bring the "metal," as the molten glass is technically called, into a condition of perfect fluidity. Under these circumstances a more readily fusible mass was

obtained by simply adding a larger quantity of potash. The quality of the glass was, however, thereby deteriorated, inasmuch as it was readily attacked by water. In order to remedy this evil a substance must be added which, whilst serving to render the glass more fusible, does not at the same time, like an excess of potash, render it soluble in water. Lead oxide was found to answer these conditions admirably.

Flint glass possesses a higher specific gravity and refractive power, as well as a higher lustre, than the other kinds of glass. It is, however, more easily attacked by acids and alkalis.

Heavy optical-glass or *crystal* belongs to this class. *Strass* contains a larger quantity of lead oxide, and has, therefore, a greater refractive power, and is used for the purpose of making artificial gems. Several other kinds of glass may be classed as belonging to this group. Thus, for instance, those in which thallium, barium, and zinc replace the lead; these also possess a high lustre, are highly refractive, and have been employed for optical purposes.

THE MANUFACTURE OF GLASS.

295 The materials employed for the manufacture of the glass are first fritted together in melting-pots. These pots require great care in their preparation and are made of the most refractory kind of fire-clay, such as that found at Stourbridge. When

Fig. 136.

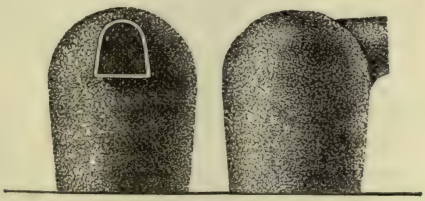


Fig. 137.

charcoal or gas is used as fuel the pots are open; when, however, coal is employed, and especially in flint-glass making, the pots are hooded or covered at the top, having a mouth in front like a muffle as seen in Fig. 137. The melting-furnace is built

of sandstone or of moulded blocks made of the purest fire-clay. The construction of the oldest form of glass-furnace as used in the time of Agricola, is shown in Fig. 138. It is hemispherical

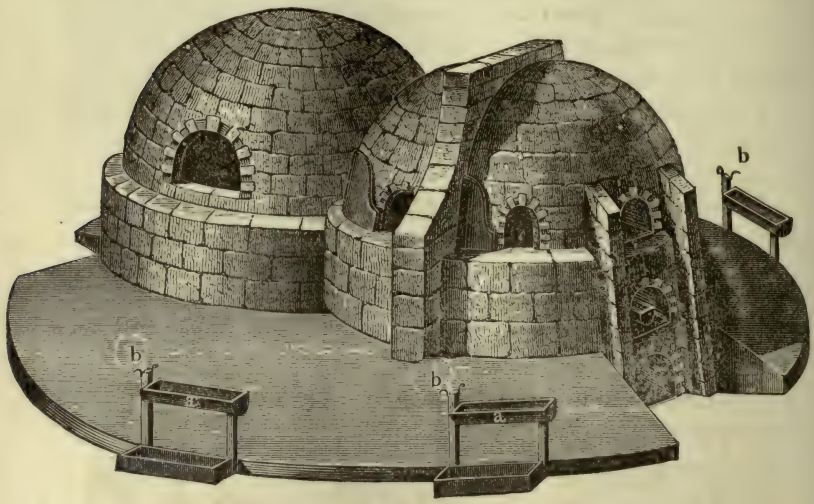


Fig. 138.

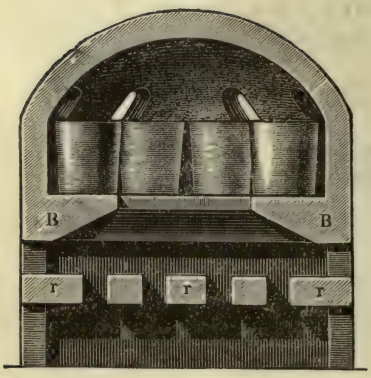


Fig. 139.

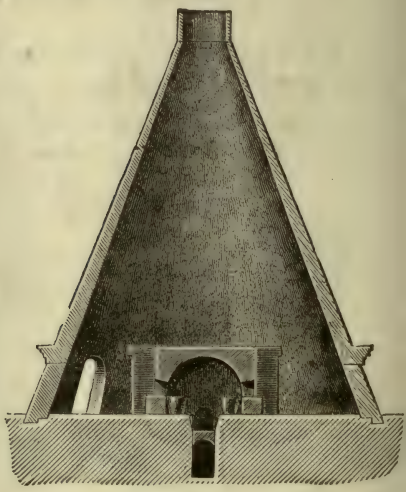


Fig. 140.

and is heated by a wood-fire placed in the lowest opening; the second opening gives access to the melting-pot, whilst the upper space serves as the annealing oven. The older glass-houses are

usually built in the form of a truncated cone, open at the top, from 60 to 80 feet in height, and from 40 to 50 feet in diameter at the base, the centre of the area being used for the melting-furnace, capable of holding from 5 to 10 glass pots or crucibles for melting the materials. In the earliest glass-furnaces wood was employed as a fuel. This was gradually replaced by coal, and this change was naturally accompanied by an alteration in the form of the furnace. The small Bohemian furnace, where

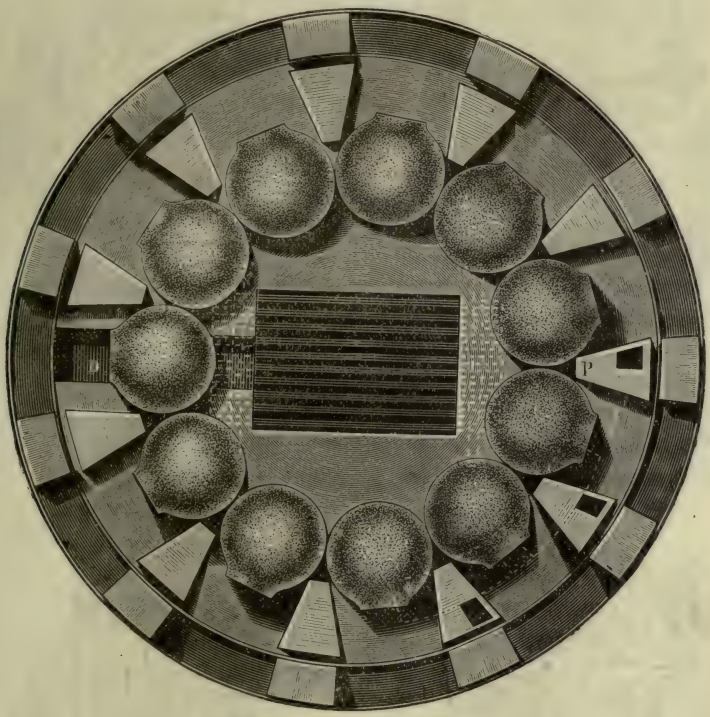


FIG. 141.

wood is employed as a fuel, shown in Fig. 139, was formerly common in Germany. In order to insure complete combustion and to bring about a sufficiently high temperature when the fuel used is coal, the arrangement shown in Fig. 140 is made use of the whole of the furnace being enclosed in a conical chimney. Figs. 141 and 142 show the construction of a modern English flint-glass furnace in plan and in vertical section. Ten large glass-pots are placed round the walls of the furnace, with

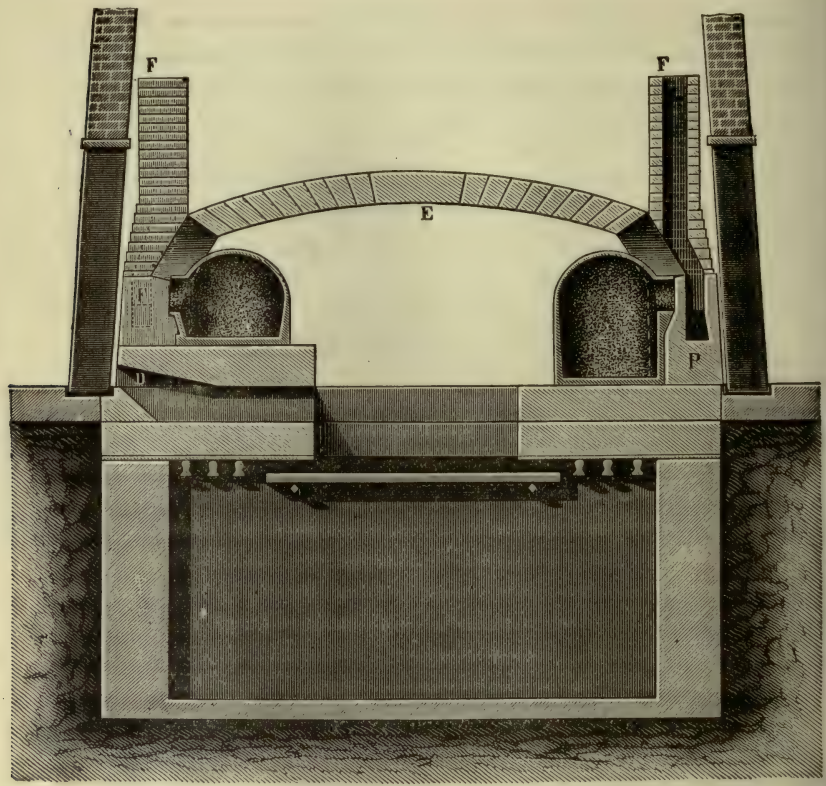


FIG. 142.

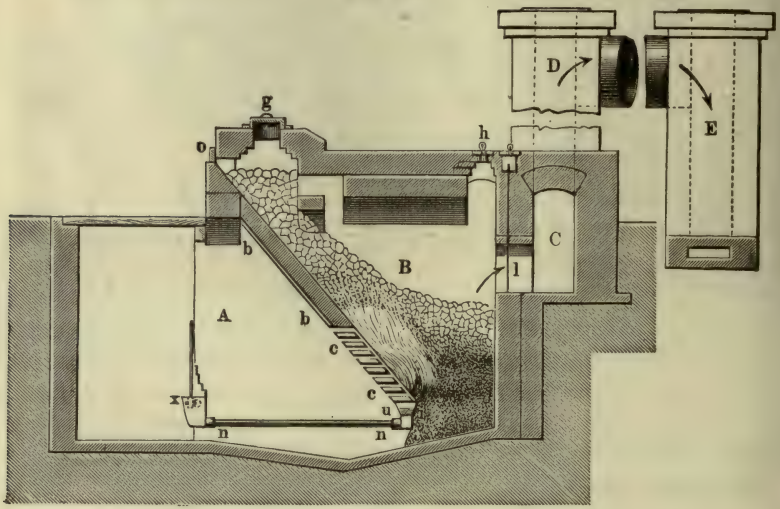


FIG. 143.

their mouths towards the outside, opposite corresponding holes in the external wall of the furnace, so that the molten glass can be readily withdrawn. A small pot is placed above the firing-hole

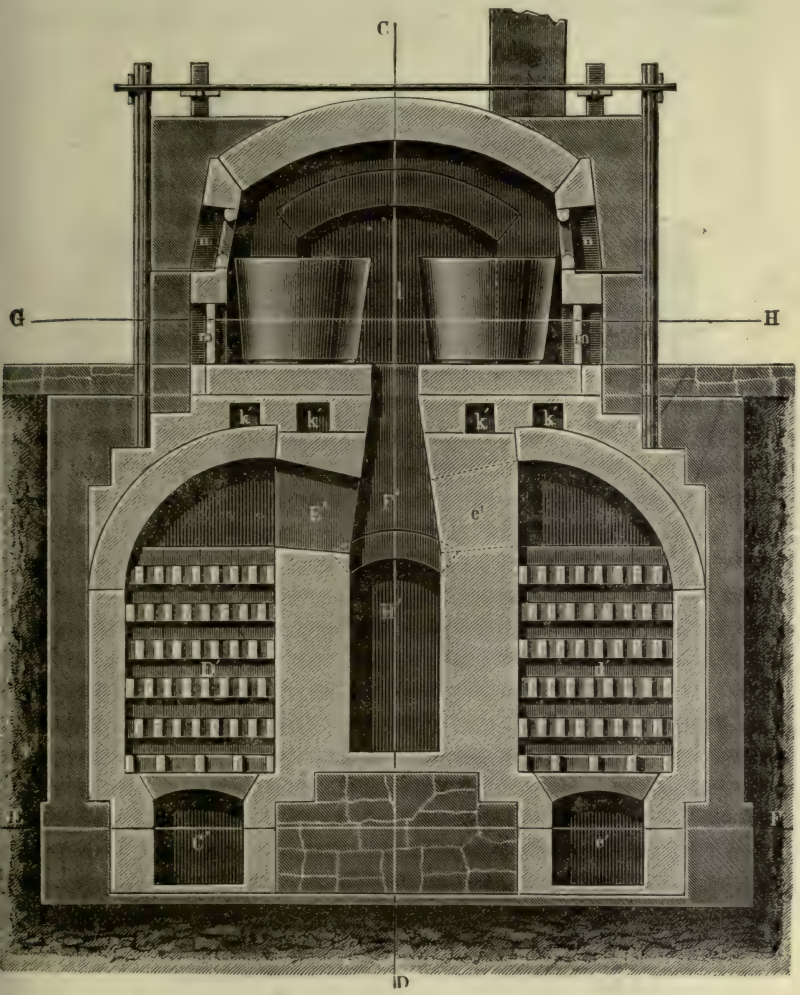


Fig. 144.

D. The grate for the coal fire is situated in the centre of the furnace and the flames striking on the arch or crown E (Fig. 142) play round each pot and find their way through the flues (F) in the pillars into the common chimney.

Amongst modern glass-furnaces that invented by Siemens is the most successful. Fig. 143 shows the gas generator, which is situated at some distance from the melting-furnace. In this the coal falls down through the opening (*g*) on to the inclined plane (*b b*), whence it passes on to the inclined bars (*c c*) of the

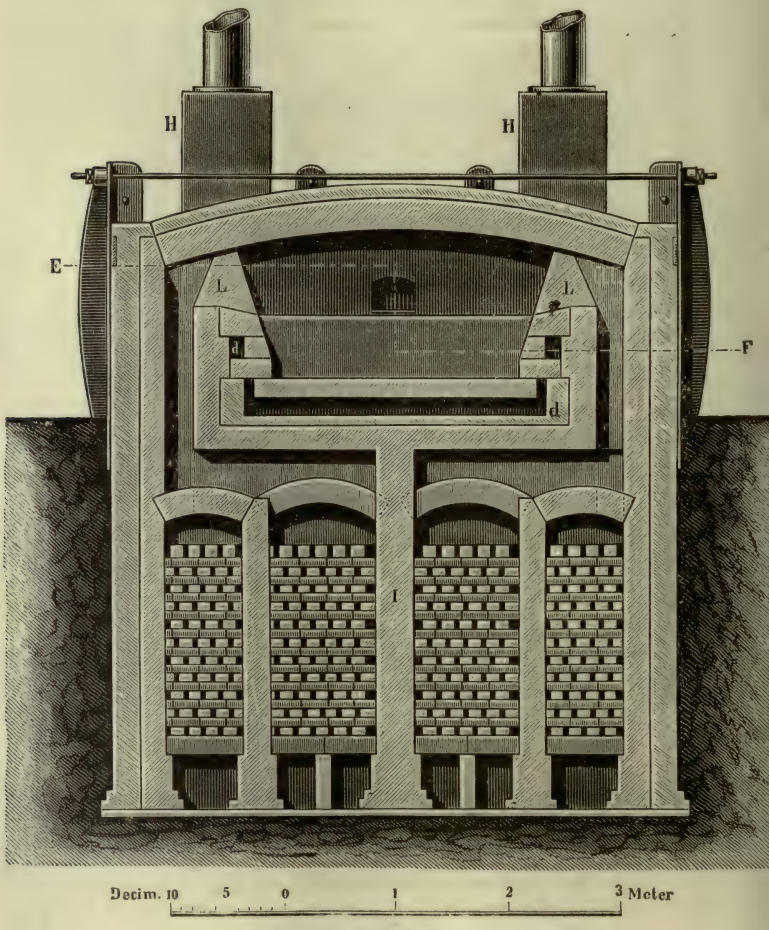


FIG. 145.

furnace. Here an incomplete combustion takes place and the coal lying above the grate undergoes dry distillation; the gases pass through the flues (C) (D) and (E), and are led into the melting-furnace, the construction of which is seen in Fig. 144. The gas passes through the flue (C′) where it is heated in the

regenerator (D′), whilst the air necessary for the combustion of the gas is allowed to enter through the air-ports (k′ k′)

Fig. 146.

Fig. 145 shows a vertical cross section, Fig. 146 a horizontal section, and Fig. 147 a vertical longitudinal section of the most

improved form of a Siemens glass-melting furnace. This furnace resembles the one last described, in having the regenerative arrangement for recovering the waste heat as shown at (D′d′) Fig. 144, but is remarkable for an improved method of construction and mode of working, the glass being placed in *tanks* instead of in *pots*. In the older forms of glass-furnace the materials are first charged into the glass-pots, then fritted and melted down and worked out completely, after which the pots are re-charged and the process repeated. Hence, a considerable loss of time and waste of fuel takes place through the intermittent nature of the work. Siemens' improvement has for its object the rendering of the process of glass-making a continuous and more uniform one. It consists of an arrangement of tanks (A), (B), (C), Fig. 147, of which (A) serves to receive the raw materials and in which they are fritted together and afterwards fused. From (A) the liquid "metal" flows into (B), the clarifying compartment, whence it again passes into (C), the working compartment, from which it can be withdrawn by the workmen in the usual manner through the doors (D, D). The compartment (A) is fed with raw materials through the charge-aperture (E) at the back of the furnace. This compartment (A) is separated from the tank (B) by a division wall (F), in which a series of passages is formed, one of which is seen at (*a*). Through these passages the melted glass flows, and from (B) it passes to the tank (C) through the passages (*b*) in the division wall (G). The sides and bottom of the tank are honeycombed with air-passages (*d d d*) through which cold air is caused to circulate by the draught produced in the chimney (H), and thus the tank-walls are maintained in a cool condition so as to enable them better to withstand any injurious action of the melted glass. The gas-ports are shown at (k k), and the heated air issues from corresponding openings passing in diverse directions over the upper edges of the wall. By this means an effectual intermixture of the combustible gas and the heated air is produced, and the air is prevented from coming into immediate contact with the surface of the melted glass in the tanks. By arranging the gas- and air-ports along the sides of the tanks the temperature in the different parts of the furnace can be regulated according to the various stages of the preparation of the glass in the several compartments.

The materials required for the formation of the glass are, if possible, always mixed with broken glass of the same kind, technically termed "cullet," for the purpose of increasing the

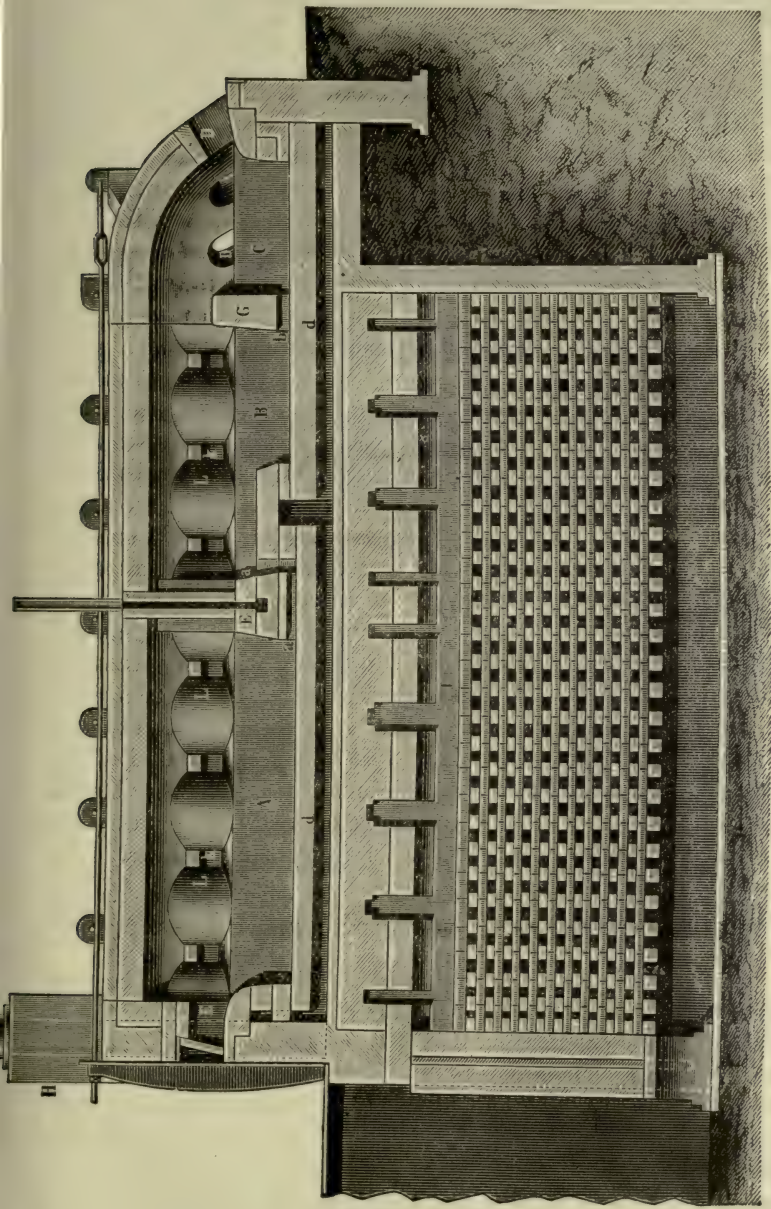


Fig. 147.

fusibility of the mass. The materials, however, are not placed in the pots until these are heated up to a high temperature. The furnace is kept very hot until the first portion of the material added has been fused, and then a second portion is introduced. When all the solid matter is dissolved, the glass is still full of small bubbles of gas, and is of a spongy nature and not yet in a fit state for working. Moreover, the surface of the melted mass is covered by a layer of salts chiefly consisting of chlorides and sulphates of potassium and sodium which have escaped perfect vitrification; this is termed *glass-gall* or *sandiver*. Formerly, when impure materials were more generally employed than is now the case, large quantities of this scum were formed. Now, however, its formation is avoided by the use of purer materials and by the addition of charcoal if salt-cake is employed, care being taken not to add an excess, as otherwise the glass assumes a yellow colour. The last process in glass-making is termed the "fining," and consists in the removal by subsidence of the heavier non-vitrified particles and the escape of the bubbles of gas to the surface. For this purpose the glass must be brought into as liquid a state as possible, and consequently at this stage of the operation the temperature is raised to the highest point. When all the gas-bubbles have disappeared and the glass-gall has become clear and colourless, the temperature of the furnace is allowed to diminish slowly, the object being to reduce the fluidity of the glass to the point at which it becomes viscid and in a workable condition. Glass is worked either by the skill of the glass-blower, for the production of the ordinary hollow- or blown-glass articles, or by casting in presses, or, lastly, by pouring the "metal" out on to iron tables and rolling it into plates. The tools described by Blancourt in his work *On the Art of Glass*, printed in London in 1699, are almost the same as those now in use.

296 *Annealing.*—All articles made of glass require to be very slowly and homogeneously cooled, for, glass being a bad conductor of heat, those portions of the glass which are on the outside solidify first, and contracting in this act of solidification leave the interior portions still warm, and these, unable to assume their natural position on cooling, are in a state of tension or condition of unstable equilibrium. Hence, glass which has been quickly cooled, cracks and falls to pieces with the slightest disturbance, such as is caused by a very slight scratch, and is liable to break when exposed to sudden changes of temperature. All glass

therefore requires to go through the *annealing* process. This consists in submitting the glass articles to a very slow cooling. The construction of an annealing oven is shown in Fig. 148. The fact of the brittleness of glass when suddenly cooled is well seen in the so-called *Rupert's Drops* (Fig. 149), obtained by allowing a little melted glass to fall drop by drop into cold water. By merely breaking off the thin point the whole mass

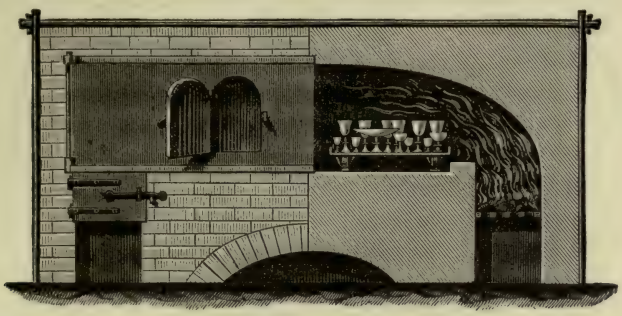


Fig. 148.

is converted with a slight detonation into a fine powder. Similarly an ordinary thick tumbler made of unannealed glass flies to pieces when the slightest scratch is made on the interior surface, as when a small piece of flint is allowed to fall into the glass.

297 *Properties of Glass.*—Pure glass is perfectly transparent and colourless. It becomes soft at a red-heat, and hence it

Fig. 149.

can be readily welded. At higher temperatures it becomes still softer and at last melts, forming first a thick and afterwards a mobile liquid, fusing the more readily, the smaller is its percentage of silica. According to its composition, glass varies considerably, both in specific gravity and lustre. Soda-lime glass has a specific gravity of from 2·4 to 2·6; the specific gravity of lead-glass rises as high as from 3·0 to 3·8, whilst the thallium-glass of Lamy reaches as high a point as 4·18. The refractive index is also dependent upon the composition. The

higher the atomic weight of the metals which it contains, the greater is the specific gravity of the glass, and the higher is the refractive index.

Kind of Glass.	Specific Gravity.	Refractive Index for the D line.
Crown-glass	2·535	1·530
Fraunhofer's flint-glass	3·135	1·707
Guinand's „ „	3·417	1·778
Lamy's thallium-glass	4·180	1·673
Diamond	3·518	2·470

It is of especial importance for the chemist that his glass vessels should satisfactorily withstand the action of chemical reagents. Ordinary soda-lime or potash-lead glass is not only attacked by acids, but is easily decomposed when placed for some time in contact with boiling water, as was first observed by Bernard Palissy. It has already been stated (vol. i. p. 26) that Lavoisier and Scheele were well aware of this solvent action of water upon glass, and that they explained this by the solution of the alkaline silicates, whilst the insoluble silica or lime-silicate floated about in the liquid. In his celebrated researches on the atomic weights of the elements, Stas[1] describes a series of preliminary experiments made for the purpose of ascertaining the kind of glass which is least subject to such deterioration. He found that glass containing lead or alumina was readily acted upon by acids, whilst Bohemian potash-lime glass being rich in silica and free from alumina withstood this action best. Such glass is, however, difficult to work from its high melting-point, and in order to obtain a glass equally capable of resisting solvents and at the same time fusible enough to enable it to be worked into the various forms of chemical apparatus, Stas replaced half of the potash in the mixture used for the Bohemian glass by its equivalent of soda, so arranging the materials that the glass possessed the following composition:—

Silica	77·0
Potash	7·7
Soda	5·0
Lime	10·3
	100·0

the molecular ratios being 9·7 SiO_2 : 1 CaO : 1·1 alkali.

[1] *Nouvelles Recherches, &c., Mem. Acad. Belg.* **35**, 216.

Emmerling, who has investigated the same subject, obtained the following experimental results.[1] The solvent action of boiling solutions on glass vessels is within certain limits proportional to the time during which the action takes place. New glass vessels are attacked to a greater extent than old ones, but the action diminishes after a while. It is also proportional to the surface exposed to the action of the liquid, but it is independent of the amount of liquid which is vaporised in a given time. Even small quantities of the alkalis attack glass violently. Dilute acids, with the exception of sulphuric acid, exert even a less corrosive action than water itself. Those salts whose acids form insoluble calcium salts act in the same way as sulphuric acid does, and their action increases with the concentration of the solution. On the other hand, those salts whose acids form soluble calcium salts attack glass less powerfully, and their action diminishes with the concentration. From these observations it follows that in order to diminish the errors which occur in quantitative analysis from the solvent action of reagents upon glass, the contact of alkaline liquids must especially be avoided, any such liquid being acidified before evaporation; it is also advisable to avoid the use of new glass vessels. The suitability of a glass vessel for chemical purposes may be judged either by the action of water alone or of acids and alkalis upon it, and it appears that the most resistant glass has the molecular composition 7·2–8 SiO_2: 1 CaO; 1·1–1·5 $(Na_2,K_2)O$.[2]

The relative proportion of soda to potash makes little difference in the resistance of glass to reagents, provided that the proper amounts of lime and silica are present. When too little lime is present, glass containing potash is much more readily attacked than that containing soda.[3]

For the manufacture of thermometers it is of great importance that the glass shall regain its original volume as rapidly as possible after it has undergone a change of temperature, since when this is not the case the zero-point of the instrument is not constant but gradually rises. Special glass for this purpose is now made under the name of Jena normal-glass which has the following composition:

[1] *Annalen*, 1869. **150**, 257.

[2] Weber and Sauer, *Ber.* 1892, **25**, 70; Mylius and Foerster, *Ber.* 1892, **25**, 97.

[3] Mylius and Foerster, *Ber.* 1889, **22**, 1092.

JENA NORMAL-GLASS.

SiO_2	67·5
Na_2O	14·0
ZnO	7·0
CaO	7·0
Al_2O_3	2·5
B_2O_3	2·0
	100·0

After being heated to the boiling-point, thermometers of this glass only show a depression of the zero of 0·06°, whilst ordinary thermometers show depressions of from 0·4 to 1·0°.[1]

298 *Devitrification of Glass. Réaumur's Porcelain.*—In 1739, Réaumur observed that if a piece of glass were surrounded by sand or gypsum and heated strongly for a considerable length of time it was converted into a porcelain-like mass, to which he gave the name of *porcélaine par dévitrification.* It was at first believed that this change was brought about by the absorption of the materials in which it was imbedded, but Lewis, in the year 1763, concluded that the formation of Réaumur's porcelain depended upon the volatilisation of the alkali contained in the glass.

This view was adopted by numerous chemists, amongst whom Dumas may be especially mentioned, under the assumption that a crystalline calcium silicate was formed which rendered the glass opaque. According, however, to the experiments of Pélouze, Benrath,[2] and Stolba,[3] the porcelain-like glass possesses the same composition as ordinary transparent glass, and Benrath in his investigation on this substance, arrives at the following conclusions. Glass which contains more silica than the amount corresponding to the formula $M_2Si_3O_7$, readily becomes devitrified. This is often noticed in working glass before the blowpipe, or even in bending tubes in a flame. Devitrified, as well as ordinary transparent glass, consists of mixtures of an amorphous and of a crystalline mass, or of mixtures of crystals which have separated out in an amorphous solidified mother-liquor. The existence of crystallised structure in ordinary glass is shown by the fact that if the surface of any unpolished glass be treated with strong aqueous hydrofluoric acid, and the etched portions well-washed with sul-

[1] See *Zeit. Instrumenten-Kunde*, 1883, **8**, 377; 1891, **11**, 330; 1892, **12** 402.
[2] *Die Glasfabrication*, 1875, p. 18.
[3] *J. pr. Chem.* 1863, **90**, 465; 1864, **93**, 118.

phuric and hydrochloric acids, the etched surface exhibits, under the microscope, a distinct finely-grained crystalline structure (Leydolt). In apparently amorphous glass then, it would appear that we have to do with a supersaturated solution which has been quickly solidified, whilst in the case of Réaumur's porcelain sufficient time has been given for the formation of larger and visible crystals. Other views are however maintained by certain chemists on this question. Thus Péligot[1] maintains that the vitreous mother-liquor contains more alkaline silicate than the crystalline portion, inasmuch as devitrified glass placed in a moist atmosphere exudes potassium carbonate in a soluble form. The same chemist also states that the melting-point of devitrified glass is higher than that of the vitrified portion.

Badly prepared window-glass, especially that rich in alkalis, becomes opaque on exposure to the air. This is due to a devitrification of the surface brought about by the action of water, carbon dioxide, and ammonia, and depends on the fact that the alkalis are separated and washed away by water, whilst an iridescent coating, consisting of a thin film of calcium silicate, remains on the surface. This iridescence of glass is especially well seen in antique glass which has been buried in the earth for a considerable length of time. A similar iridescent surface on glass is now produced artificially by heating ordinary glass under pressure in contact with hydrochloric acid.

OPAQUE AND COLOURED GLASS.

299 Transparency is certainly the most important property of glass, and yet for some purposes translucent or even opaque glass is useful. The ordinary opalescent or enamelled glass is either soda-glass or flint-glass which has been rendered opaque by the addition of an insoluble powder such as bone-phosphate or mineral-phosphate. Cryolite has also been employed in place of phosphate, giving rise to a material manufactured in Pittsburg, U.S.A., and known under the name of hot-cast porcelain. Ellis describes the manufacture of milk-glass of this kind as consisting in fusing together 1 part of cryolite with from 2 to 4 parts of white sand, whilst, according to Williams, an addition to this mixture of 9 per cent. of zinc oxide improves the result.

[1] *Le Verre*, Paris, 1877, p. 45.

Instead of cryolite, fluor-spar or sodium aluminate may be employed.

Another opaque variety of glass is known under the name of *enamel*. This name originally signified lead-glass rendered white by oxide of tin. At the present day several oxides are employed for this manufacture, such as those of antimony and arsenic, as well as permanent white or sulphate of barium. Enamel is used especially for covering the surface or for "enamelling" iron vessels used for cooking and other purposes.

The ancients were well acquainted with the mode of preparing *coloured glass*, and not only did they colour it in mass, but they were conversant with the process of "flashing," that is of coating a white glass with coloured glass. An example of this is seen in the celebrated Portland vase. The white figures of Peleus and Thetis have been obtained by cutting away, on the background, the white surface which originally covered the whole vessel. Figures on flashed glass are still prepared in the same way by cutting away the outer coating, and thus allowing the colour of the lower layer to be seen. The process of flashing is also employed when the colouring matter would be too intense if the whole mass were coloured, and thus by varying the thickness of the outward crust of coloured glass differences in tint can be brought about. Blown-glass can be coloured either on the exterior or interior surface. In the first case the glass-blower brings the requisite quantity of colourless glass on to his blowpipe, and dips this into the molten coloured glass so as to cover it with a thin film; whilst in the other case the coloured is covered with the colourless glass.

Ruby Glass.—The older chemists were acquainted with the fact that glass could be coloured a ruby-red tint by means of gold compounds. Thus Neri describes a method of preparing ruby glass by adding to the glass-maker's materials the residue from the evaporation of a solution of gold in aqua-regia. General attention, however, was drawn to this subject in the 17th century, after the discovery of the *purple of Cassius*, obtained as a dark red powder by mixing the chlorides of gold and tin (p. 400). Amongst other chemists, Kunkel occupied himself with the preparation of this gold pigment, and obtained from the Elector Frederic William the sum of 1,600 ducats for his experiments.

In his *Ars Vitriaria Experimentalis* he says: "There was a

certain *Doctor medicinæ*, by name Cassius, who discovered the *præcipitatio Solis cum Jove:* to this perhaps Glauber may have given occasion, but I leave this undecided. The aforesaid Doctor Cassius endeavoured to bring it into glass, but when he tried to form a glass with it, or when he took it out of the fire it was as colourless as crystal, and he could not bring any permanent red out of it. He may, however, have observed, being a man curious about these things, amongst the glass-blowers that when they softened glass in the flame of the lamp the colour underwent a change. Thus he came to try the same plan with gold glass, and obtained a splendid ruby colour. When I learnt this, I set to work at once, and I know best what trouble I had to hit the proper composition, and to find out how to get it always red."

The secret which is involved in the above words is explained in the *Laboratorium Chymicum*, which appeared after his death: "This ruby glass possesses the property that when the glass is melted with the ☉ (gold) it comes out of the fire as clear as crystal, and in order to become red must be heated again in a mild fire."

Ruby glass, now prepared by the addition of the purple of Cassius or of gold chloride, possesses the property above described and remains perfectly colourless when quickly cooled; but when heated to the point at which it becomes soft, the whole mass attains a ruby-red colour. By the addition of tin or silver compounds, a variety of tints between a rose-red colour and a red-purple colour can be obtained. The exact nature of the gold compound which produces the ruby-colour in glass is not yet known, nor can we explain why the glass becomes red only on a second heating. Some suppose that the colour is due to metallic gold in so finely-divided a state that the substance only allows red light to pass through it. The amount of gold contained in ruby glass is very small, amounting to from 0·05 to 0·06 per cent.

300 *Copper Ruby Glass.*—Cuprous oxide also colours glass a fine and intense red, but inasmuch as this compound readily undergoes oxidation and as cupric oxide imparts to glass a light green colour, a reducing agent such as iron-scale is added to the materials. Oxidation is also prevented by poling the molten mass with pieces of fresh wood. The mass on cooling appears of a light green colour, but becomes red on re-heating. The preparation of this glass was also understood in early times. Klap-

roth found both copper and iron in a sample of old Roman glass, and in the beginning of the 17th century Neri described a method of calcining copper in order to colour glass, and stated that iron-filings, iron-scale, or other reducing agents must be added in order that the colour might come out a bright red. Kunkel also employed himself with the preparation of this glass, but in later times the art of producing red glass without purple of Cassius was lost, and it was not until the year 1828 that Engelhardt examined the question and obtained a prize which the Berlin Polytechnic Society had offered for the discovery, since which time the method has been generally practised. Cuprous oxide possesses a very strong colouring power, and for this reason copper-ruby is generally used for flashing or casing. Ferric oxide (colcothar) also imparts a red colour to glass, but one less brilliant than the two preceding ones.

Yellow Glass is prepared by the addition of potassium antimoniate or of antimony-glass, a fused and imperfectly oxidised sulphide of antimony, which imparts to glass a topaz-like tint. Other yellow colours are obtained by the use of silver chloride and silver borate. Organic bodies also impart a yellow tint to glass. This must have been observed by Thomas Aquinas, who describes a mode of preparation of artificial topaz by placing a piece of aloe-wood over the vessel in which the glass is melted. It was formerly believed that this brown colour was due to carbon. Splitgerbe has, however, lately shown that it is caused by the presence of the sulphides of the alkali metals obtained by reduction from the sulphates contained in the material used for glass-making.

301 *Green Glass* is obtained by the addition of cupric oxide, and this fact was known to the ancients, the above substance being found in antique glass. According to Seneca, Democritus of Abdera was acquainted with a method for producing the emerald artificially, and Theophrastus, about 300 B.C., described a mode of colouring glass green by means of copper. Other green tints are obtained by the addition of oxide of chromium and ferrous oxide. The latter, however, gives a dull bottle-green colour.

Cobalt oxide colours glass a fine *blue*, and this oxide has been used from early times for this purpose. Davy found cobalt in all the antique blue glass which he examined.

The *violet* colour of glass is due to manganese oxide. This is obtained by the addition of black oxide of manganese and nitre.

A fine *black* opaque glass is obtained by the addition of sesquioxide of iridium to colourless glass, and a common black glass is prepared by adding large quantities of ferric oxide, with which copper oxide or cobalt oxide is frequently mixed.

Strass and Paste.—The property of glass to attain a variety of tints by the addition of various metallic oxides is made use of for the production of artificial gems or paste, and this art has now attained such perfection that it is difficult even for an adept to ascertain upon mere inspection whether a gem is real or artificial. The discrimination can, however, be made at once by determining the hardness of the stone with a good file, inasmuch as the artificial are much softer than the natural gems. Strass is employed for the basis of paste, and is distinguished by its high refractive power and bright lustre. According to Donault-Wieland *topaz* is formed by adding to 1000 parts of strass, 40 parts of antimony-glass, and 1 part of purple of Cassius. *Ruby* is obtained from the ingredients of the topaz mixture by fusing 1 part of this with 8 parts of strass and allowing the fused mass to remain at the temperature of the furnace for thirty hours. *Emerald* is prepared by fusing 1000 parts of strass, 8 parts of cupric oxide, and 0·25 part of chromium oxide. *Sapphire* can be made by the addition of 15 parts of cobalt oxide to 1000 of strass; *amethyst* requires the addition of 8 parts of manganese dioxide, 5 of cobalt oxide, and 2 of purple of Cassius; whereas the *beryl* or *aqua-marine* is prepared by adding 7 of antimony-glass and 0·4 of cobalt oxide to the 1000 of strass, and *Syrian garnet* or *carbuncle* requires 500 of antimony-glass and 4 parts each of manganese dioxide and purple of Cassius to the same quantity of strass. These special tints can, however, be readily varied at pleasure.

302 *Avanturine Glass or Artificial Avanturine.*—This material is a reddish or greenish glass filled with minute crystals or spangles, which have a golden lustre. It has received its name from a rare form of quartz which occurs in Spain and the Altai, containing spangles of mica or other mineral. Artificial avanturine is more beautiful than the natural mineral, and the method of its manufacture is said to have been discovered by chance in the 13th century by Briani in Venice. The artificial avanturine was largely employed for the preparation of ornaments and especially for Venetian mosaic work. The details of its preparation were long kept secret, and the process was only carried out by a few of the highest Venetian families. In the year

1847 Pettenkofer[1] investigated the preparation of the antique hæmatine, an opaque red glass, and in the preparation of this material he obtained by accident artificial avanturine. Many not wholly successful attempts have been made to determine the exact conditions under which the avanturine is thus formed, and the Venetian manufacture still maintains its supremacy. Avanturine is a white soda-lime glass, containing an excess of alkali, and coloured red by cuprous oxide, containing an enormous number of minute spangles of metallic copper. According to Hautefeuille, a green cupric glass is first prepared; to this iron-filings are gradually added until it becomes red and opaque; hæmatine glass is thus formed, which is then well covered with ashes, and allowed gradually to cool, when the artificial avanturine glass is formed.

White and coloured *enamels*, largely used for the preparation of thermometer scales, as well as Mosaic work, usually consist of common flint-glass, which is intensely coloured with the above-mentioned oxides and then poured on to the metal, to the surface of which it adheres.

303 *Toughened Glass.*—The fact that glass can be toughened was discovered by De la Bastie. It is obtained by dipping glass heated almost to redness into oil, also heated to 300°, and allowing it then to cool gradually. Sheets of glass are also toughened by allowing them to cool between plates of heated metal. The glass thus prepared is much less brittle, and better able to withstand sudden changes of temperature than ordinary glass. Table-glass thus toughened is not readily broken when thrown on to the ground. If, however, it be thrown from a great height or with great force, it breaks into fine splinters. Although a crack may occur in a vessel of toughened glass without the whole of the mass breaking up, yet it cannot be cut with a diamond; from this it would appear that the molecules of toughened glass are in a condition somewhat similar to that of the Rupert's drops.

304 *Etching of Glass.*—The etching of glass with hydrofluoric acid was known in the 17th century, but it is only recently that this process has been employed for the decoration of glass, and now etched glass is much used in place of the more expensive cut-glass. Gaseous hydrofluoric acid as well as many soluble fluorides produce an opaque surface on glass, but the surface of glass etched with liquid hydrofluoric acid presents,

[1] *Dingl. Polyt. Journ.* **145**, 122.

according to the concentration of the acid, a more or less transparent character. According to Tessié de Mothay and Maréchal, the best mode of obtaining opaque- or ground-glass by means of hydrofluoric acid is to employ a bath made of 1000 parts of water, 250 parts of crystallised double fluoride of hydrogen and potassium, 250 parts of commercial hydrochloric acid, and 140 parts of potassium sulphate. This last salt renders the fluorides of calcium and lead which may be formed less soluble, whereby they are separated out in the crystalline form on the portions of the glass which have been etched and thus tend to render the surface more opaque. Various other mixtures of fluorides and acids are also employed.

The matt-surface is now usually produced on glass by exposing it to a sand blast, the parts which are to remain smooth being protected by paper.

POTTERY, PORCELAIN, AND EARTHENWARE.

305 The potter's art is one of the oldest in existence. The Egyptians were well acquainted with the means of glazing ware made of burnt clay, as well as with the art of enamelling in colours. Amongst European nations the Etruscans were especially celebrated in early times for their proficiency in the manufacture of painted pottery-ware, and in Pliny's time several towns in Greece and Italy were well known for the beauty and artistic taste of their vases, urns, and other pottery wares.

Porcelain was not known to the Romans, although the Chinese have manufactured it for ages, and the Egyptian tombs contain remains of vessels made of a material closely allied to porcelain. The art of glazing pottery with the oxides of lead and tin was generally practised in Europe during the Middle Ages, and we find a description of the process then adopted in the writings of the alchemists Peter Bonus and Albertus Magnus, at the beginning of the thirteenth century. In the following century the potter's art made great strides. Agricola published many receipts concerning this manufacture; amongst others, he states that not only a mixture of litharge with tin oxide gives a good glaze, but that the former oxide may be employed alone for this purpose.

Amongst those who have been most active in promoting the progress of the ceramic art the name of Bernard Palissy stands

pre-eminent. Devoting himself with self-sacrificing assiduity to the production of glazed and coloured faience, Palissy laid the foundation of modern art pottery. His numerous writings published during the latter half of the sixteenth century, spread a knowledge of his experimental methods throughout Europe; but his works *L'Art de Terre et des Terres d'Argile* are confined to a description of the manufacture of earthenware; it was not until the year 1709 that the method of making porcelain was discovered by Bötticher, and in the following year the celebrated porcelain manufactory at Meissen, in Saxony, was established.

The mode of preparation of the Meissen porcelain was naturally kept secret, and the King of Prussia instructed the celebrated chemist Pott to determine the nature of the materials used, and he being unable to obtain any satisfactory information respecting the materials there employed, was obliged to investigate the properties of those substances which might possibly be used in the manufacture, mixed in varied proportions, and for this purpose Pott is said to have made no less than 30,000 experiments. To these we are mainly indebted for the establishment of the reactions which occur when various minerals are heated, and much valuable information applicable to the manufacture of porcelain was thus obtained. About the same time Réaumur endeavoured to determine the secret of porcelain-making, and found that it is produced by the union of two earths, one of which is fusible, whilst the other fuses only at a very high temperature, so that by the firing of both together a translucent mass is formed.

His investigations were taken up in the year 1758, by Lauraguais, D'Arcet, and Legay, in France, and by the help of Macquer they succeeded in re-discovering the art of porcelain-making, and in the year 1769 the celebrated porcelain manufactory of Sèvres was founded.

Even up to the beginning of this century real porcelain was a material of great rarity and value. At the present day, however, it is cheap, and employed for making the most ordinary articles of every-day use.

306 *Hard porcelain or True porcelain* is distinguished by its fine and hard translucent structure, and is with difficulty attacked by chemical reagents. According to Emmerling's experiments water and acids, even when boiled, have next to no action on porcelain, and it is attacked by alkalis less powerfully than glass, and hence in chemical and analytical operations the

use of porcelain is much to be preferred to that of glass. Porcelain also stands rapid alteration of temperature without cracking, and this property is one of extreme value to chemists, whilst its beauty, and the fact that its surface is capable of taking colours which will stand firing, render it of great importance in the manufacture of objects of art. The principal material of which porcelain is composed is *kaolin* or *China-clay*, an infusible plastic substance derived from the decomposition of felspar or felspathic rocks. Pure felspar has the composition $(K,Na)AlSi_3O_8$, whilst pure kaolin is represented by the formula $H_2Al_2Si_2O_8 + H_2O$. This substance is a distinct mineral species, and frequently occurs crystallised in four- or six-sided tablets belonging to the rhombic system. More commonly, however, it is found as a white or yellowish-white amorphous mass, and contains a small quantity of ferric oxide, or magnesia. Kaolin is found in China, near the Kauling Mountains, whence its name is derived, and in other places. In Europe the finest China-clay is found in Limoges, and it is from this that the celebrated Sèvres porcelain is made. Good China-clay is likewise found in Cornwall, Saxony, various localities in America, &c. Ordinary clay consists of a mixture of kaolin with calcium carbonate, magnesium carbonate, ferric oxide, silica, and organic matter. The following table gives the composition of some of the clays:—

	Silica.	Alumina.	Ferric Oxide.	Lime.	Magnesia.	Alkalis.	Water.
Kaolin from China ...	50·63	32·74	2·64	0·50	0·27	2·52	10·01
,, ,, Yrieux ...	48·37	34·95	1·26	—	—	2·40	12·62
,, ,, Aue ...	46·00	39·00	0·25	—	—	—	12·74
,, ,, Cornwall	46·38	38·60	—	3·47	—	1·77	9·08
Cornwall clay	45·82	39·42	—	—	—	—	14·26
Strassburg	66·70	18·20	1·60	—	0·60	—	12·00
Stourbridge...	63·30	23·30	1·80	0·73	—	—	10·30
Dorsetshire blue clay	46·38	38·04	1·04	1·20	—	—	13·44

307 When strongly heated, felspar fuses to a colourless glass, owing to its containing alkali silicates. Clay, however, only bakes together under the influence of heat, forming a hard but

porous solid. It is to this property, and also to that of its forming with water a plastic mass, that clay owes its employment in pottery. In the manufacture of porcelain the infusible kaolin is mixed with a frit, flux, or fusible material, consisting of a fusible silicate. This on fusion penetrates into the pores of the heated clay, producing a hard, homogeneous, translucent, lustrous mass. The name porcelain is derived from a Portuguese word *porcellana*, a shell which is similar in general appearance to porcelain. The ordinary flux employed is felspar, but sometimes quartz, chalk, or gypsum is added. The relative amounts of these materials which are used depend upon the nature and composition of the kaolin employed, and this varies according to the locality in which it is found. The following table gives mixtures employed in a few of the more important manufactories:—[1]

Sèvres.—The materials employed in the manufacture of this celebrated porcelain are always mixed in proportions which give a mass having the following percentage composition:—

Silica.	Alumina.	Lime.	Potash.
58·0	34·5	4·5	3·0

The ingredients which are employed in different years for the production of this mass are, however, very different, as is seen in the following:—

	1836	1837	1843
Kaolin	70·0	64·0	48·0
Argillaceous kaolin . .	9·2	18·0	48·0
Quartz „ . . .	12·0	15·0	—
Quartz sand from Aumont	5·3	0·1	—
Washed chalk	3·5	2·9	4·0
	100·0	100·0	100·0

Vienna.—The ingredients used for the preparation of the well-known Viennese porcelain were in 1815 as follows:—

Passau kaolin, No. 1 . . .	101
„ „ No. 2 . . .	111
Kaolin from Zettlitz . . .	98
Quartz	18
Felspar	57
Lime	15
	400

[1] Knapp, *Chemical Technology.*

Nymphenburg.—This porcelain is made without felspar, and is a lime porcelain made of the following ingredients:—

Passau Kaolin.	Bodenmais Quartz.	Marble.
100	40	10 = 150.

When a mixture has proved to be successful each manufacturer adheres strictly to his special receipt, not only because an alteration in the proportions would render a different temperature necessary for burning, but especially because this would also entail a greater or less shrinking of the mass, for all clays, when burnt in the kiln, undergo a certain amount of shrinking, and this varies according to their composition. It is, however, extremely difficult so to arrange the materials that the shrinking shall take place to the same extent in different mixtures; and as the manufacturer has frequently to prepare his wares to pattern, it is necessary to keep to one mixture. In the use of felspar, quartz, or chalk the most important point to be ascertained is their purity, whilst in the case of clay the determination of its fire-resisting power has also to be made. On this subject Bischof and Richters[1] have published elaborate investigations, to which we must refer the reader.

The greatest care has to be taken in the thorough mixing of the materials, and in obtaining them in a very finely-divided state. For this purpose the clay is ground and levigated with water, and the water got rid of by careful pressing through bags. In this way the mass of porcelain clay is brought to the right state of consistency. It is then well mixed by kneading, and is allowed to remain for a considerable length of time in a moist place, so that the organic matter contained in the clay undergoes putrefactive decomposition: this seems to increase the plasticity of the mass; but the exact action which takes place under these circumstances is not well understood. The material is then either worked up on the potter's wheel, or brought into the requisite shape by pressing into moulds, and the objects thus prepared are allowed to dry at the ordinary temperature before firing. True porcelain is glazed with a felspathic glaze, which must be colourless, smooth, and have a glassy lustre. The composition of porcelain glaze is seen in the following table:—

Sèvres.	Meissen.		Berlin.	
Pure ground felspar.	Quartz	37	Quartz	43
	Kaolin from Seilitz	37	Kaolin from Morl	31
	Lime	17·5	Gypsum	14
	Broken porcelain	8·5	Broken porcelain	12
		100·0		100

[1] C. Bischof, *Dingl. Polyt. Journ.* **159—211**; Richters, *ibid.* **191—197.**

Before glazing, the porcelain requires to undergo a preliminary process of baking, it being placed, for this purpose, in the upper portion of the porcelain kiln. The fired goods are then dipped into water containing the finely-divided glaze in suspension. They are then dried and again exposed to a higher temperature in the porcelain kiln, which consists essentially of a high reverberatory furnace. The flame and hot gases surround the earthenware "seggars," or infusible crucibles, in which the porcelain ware is placed to protect it from the smoke and direct action of the flame. When the temperature has reached its maximum, the kiln with its contents is bricked up, and the whole allowed to cool very slowly. This annealing process is necessary, as the glaze forms a true glass, and if the heated mass were quickly cooled the porcelain would be brittle from the unequal tension of its different parts.

308 *Painting on Porcelain* is a branch of the art of glass-staining, the only difference being that in the latter case the colouring matter is viewed by transparent light, whereas in the former case the colours are seen by reflected light. The same substances are employed for painting upon porcelain as are used in colouring glass. They are divided into two classes: (1) Those which are not destroyed at the temperature of the porcelain kiln, and can be painted on the ware below the glaze,—these are termed refractory colours, and include cobalt-blue, chrome-green, the brown produced by oxide of iron or manganese, chromate of iron, &c., and uranium black; and (2) those colours which are injured when heated above a certain temperature, —these are termed muffle-colours, because they are fixed on the ware by a separate firing at a lower temperature in a muffle and not in the kiln. Muffle-colours are put on over the glaze. The following substances are used as muffle-colours: oxides or salts, such as iridium oxide, cupric oxide, cuprous oxide, chromate of lead, silver chloride, purple of Cassius, &c., and as flux for these are employed, quartz or sand, borax or boric acid, felspar, litharge and red-lead, nitre and the carbonates of potassium and sodium.

309 *Tender or Fritted Porcelain.*—This form of porcelain was first prepared in 1695, by Morin in St. Cloud. The mass resembles that of true china, but the glaze is much more fusible than the felspathic glaze used for the latter material and it is, therefore, less able to resist the high temperature of the porcelain kiln than true china. This is the kind of porcelain specially manufactured in England. The materials employed in this manu-

facture are: (1) The mass or body composed of Cornish stone, China-clay, or decomposed pegmatite. (2) The frit or fusible material used to bind together the China-clay. This consists of bone-ash or mineral phosphate with, sometimes, the addition of borax. (3) The glaze is much more fusible than the mass and consists of bone-ash, sand, borax, potashes, and lead oxide. The difference in fusibility between the mass and the glaze constitutes the main difference between fritted porcelain and true porcelain. The following are mixtures in use for English china:—

	I.	II.	III.	IV.
Bone-ash . .	47	41	36	47·3
Cornish stone .	31	30	21	—
China-clay . .	22	29	21	33·8
Blue Dorset clay	—	—	12	—
Felspar . . .	—	—	—	18·9
	100	100	100	100·0

The glaze used for English table-ware consists of:—

Cornish stone . . .	34
Chalk	17
Ground flint . . .	15
Borax	34
	100

These materials are fritted, then ground and mixed with 10 per cent. of Cornish stone and 20 per cent. of white-lead.

Parian or Carrara biscuit-ware is a white unglazed porcelain, less fusible than ordinary tender porcelain and largely used for the preparation of statuettes.

Stoneware is distinguished as fine and ordinary stoneware, and is related to porcelain, inasmuch as it is also prepared from clay fritted together with a flux, and therefore consists of a homogeneous dense mass which is distinguished from porcelain by its opacity, due to the fact, that the frit or fusible porcelain is not diffused throughout the mass as is the case with porcelain. The materials used are the plastic clays and pipe-clays found in large quantity in the coal measures, and these are mixed with a felspathic glaze. The glaze employed sometimes contains lead and borax. The frit is always contained in larger

proportion in stoneware than in porcelain, and hence it does not require to be exposed to so high a temperature in the process of baking. Stoneware is therefore a cheap and effective substitute for porcelain, as it is produced at a lower cost and at the same time can be more easily worked.

Semi-porcelain.—This is a fine kind of stone-ware, prepared from a white plastic clay, to which ground quartz, or flint, or even felspathic stone, is added in the requisite quantity. After the first burning it is porous and adheres to the tongue. It is then glazed with a transparent glaze consisting of borax, quartz, soda, and oxide of lead. Semi-porcelain is made from an impure clay, and the peculiar colour which it possesses is covered by this white opaque enamel.

310 *Earthenware.*—This material differs from the foregoing, inasmuch as the mass before glazing is porous and earthy. Earthenware is made from a coloured plastic clay which, on burning, forms a hard porous mass, and in order to diminish the shrinking it is frequently mixed with marl. It is glazed by throwing common salt into the kiln when the burning is nearly complete. This is volatilised and decomposed by the aqueous vapour and the products of combustion, with formation of hydrochloric acid and soda, which latter unites with the clay to form a sodium aluminium silicate. Salt-glaze ware is largely used for drain-pipes, pipes for conveying acid gases and liquids, and for vessels for storing acids, as well as for ordinary domestic use.

Faience is an opaque, porous, generally soft body pottery, always coloured, with either a glaze rendered white and opaque by tin or sometimes by calcium phosphate (*faience émaillée*) or else having a transparent lead glaze. In this latter case a slip of finer clay generally covers the coarse body. It was known and manufactured in the 9th century by the Arabians, and the knowledge of the manufacture passed with the Moors into Spain, and established itself in the island of Majorca, whence the name *Majolica* is derived, being the old Tuscan name for this island. The same industry in Italy was named faience from the name of the town of Faenze in the States of the Church, where it was established in the 13th century, and flourished until the 15th. In France, the manufacture was commenced by Bernard Palissy, in the 16th century.

311 *Common Pottery Ware* is made of the most impure forms of clay, coloured brown-yellow or red with ferric oxide and other oxides. In many cases it also receives an easily fusible lead

glaze obtained by mixing lead oxide, or even ground galena, with the clay.

The various kinds of melting crucibles which are made of clay have a special interest to the chemist. These require to be made of material which will stand a very high temperature without softening or breaking up, and capable of withstanding rapid changes of temperature. The well-known Hessian crucibles are made of a clay containing about 71 parts of silica, 25 of alumina, and 4 of oxide of iron, and this is mixed with one-third to one-half its weight of quartz sand.

GALLIUM. Ga = 69·4.

312 This metal, the eka-aluminium of Mendeléef (p. 61) was discovered in 1875 by Lecoq de Boisbaudran by means of spectrum analysis. He found the new element in the zinc-blende of Pierrefitte in the Pyrenees and patriotically gave to it the name which it now bears. It is also found in the blende from other localities. Thus a yellow transparent blende from Asturias and a black blende from Bensberg contain it; and that from Bensberg, although the richest, contains only 16 mgr. of gallium per kilo. All other zinc ores which have been tested for gallium have either yielded negative results, or have contained mere traces of the new metal.

In order to prepare gallium, the ore, according to its physical character, is dissolved either in aqua-regia, hydrochloric acid, or sulphuric acid, and the solution decomposed by means of metallic zinc. The precipitate thus thrown down, which contains most of the foreign metals present in the blende, is then treated with hydrochloric acid, and the liquid again precipitated with zinc in the cold. As soon as the evolution of hydrogen becomes feeble, the solution is poured off from the precipitate and saturated with sulphuretted hydrogen, the precipitate filtered off, the excess of sulphuretted hydrogen driven off, and the liquid fractionally precipitated with sodium carbonate in the cold until the precipitate thrown down no longer exhibits the gallium line when examined with the spectroscope. It is then dissolved in sulphuric acid, gently evaporated until the excess of sulphuric acid is almost completely removed, the residue treated for some time with cold water, and the solution diluted with

water, and then heated to boiling, when basic gallium sulphate separates out, which must be filtered off whilst hot. This precipitate is dissolved in a small quantity of sulphuric acid; to this liquid a slightly acid solution of ammonium acetate is added, sulphuretted hydrogen passed through to saturation, the solution filtered, and the filtrate, diluted with water, heated to boiling, the precipitate which forms being washed with boiling water. This is then dissolved in a small quantity of sulphuric acid, a slight excess of alkali added, and the alkaline solution submitted to electrolysis. Metallic gallium is thus deposited on the platinum pole, and in order to obtain it in the perfectly pure state it is treated with warm dilute nitric acid free from chlorine. Sixty-two grms. of gallium were exhibited in the Paris Exposition of 1878, having been prepared from 2,400 kilos. of blende by Lecoq de Boisbaudran and Jungfleisch.[1]

Metallic gallium possesses a bluish-white colour, and has the remarkable property of fusing at 30°·1. The molten metal possesses the colour of silver, and remains liquid for many weeks at the ordinary temperature, and even when exposed to 0°. If, however, the globule be touched with a small fragment of solid gallium it at once solidifies forming pyramidal crystals, probably belonging to the monosymmetric system.

Gallium is tough, and may be cut with a knife; the molten metal, when brought on to glass, covers the surface with a bright mirror-like deposit, and oxidises on exposure to the air. It is not volatile at a red-heat, and only a thin film of oxide is formed on the surface. Its specific gravity is 5·9, and its specific heat 0·080. It is easily soluble in dilute hydrochloric acid and caustic potash with evolution of hydrogen. It is scarcely attacked by dilute nitric acid in the cold, but on heating it slowly dissolves with evolution of red vapours If a neutral solution of gallium chloride be warmed with zinc, gallium oxide or a basic salt separates out, but not the metal.

Gallium Oxide, Ga_2O_3, is a white mass, which is reduced to the metal by hydrogen at a bright red-heat. The hydroxide is a white precipitate insoluble in water, but readily soluble in potash, and somewhat less so in ammonia.

[1] *Compt. Rend.* 1878, **86**, 475.

SALTS OF GALLIUM.

313 *Gallium Trichloride*, $GaCl_3$.—Like aluminium, but unlike indium, gallium yields the trichloride when heated in hydrogen chloride as well as in chlorine, long needle-shaped crystals being deposited in the tube close to the flame. It is a very deliquescent substance, and dissolves in a small quantity of water to form a clear liquid, which on the further addition of water becomes turbid from deposition of a basic salt. It melts at 75°·5 and boils at 215-220°. The vapour density of gallium chloride as determined by the air-replacement method, is 6·1 between 440–606°, and corresponds to the formula $GaCl_3$. Like aluminium chloride its density near the boiling point is somewhat higher than this, being 8·8 at 350°.[1]

Gallium Dichloride, $GaCl_2$, is obtained by the action of the metal on the trichloride and melts at 164° forming a limpid refractive liquid which boils at 535°. The specific gravity of its vapour is 4·8 at 1000°, corresponding to the formula $GaCl_2$.

Gallium Sulphate is also very soluble, but non-deliquescent. It combines with sulphate of ammonium to form an alum $Ga_2(SO_4)_3 + (NH_4)_2SO_4 + 24H_2O$, which crystallises in combinations of the cube and octohedron. If its solution be boiled a precipitate is produced consisting probably of basic sulphate.

Gallium Nitrate is also a soluble well-crystallised salt.

The best means of detecting gallium is by the spark-spectrum of the chloride or other salt. This consists of two violet lines, (4171, 4031) of which the brightest, Gaα, lies a little more towards the blue than the line Inβ, and the second Gaβ rather more towards the violet than Kβ. In the non-luminous gas-flame the chloride gives only a very slight indication of the line Gaα.

The atomic weight of gallium has been determined by Lecoq de Boisbaudran[2] by igniting the ammonium alum, and also by dissolving the metal in nitric acid and igniting the residue, the oxide obtained in both cases being weighed. The first determination gave the atomic weight 69·6, and the second 69·2 (O = 15·88).

[1] Nilson and Pettersson, *Journ. Chem. Soc.* 1888, i. 824.
[2] *Bull. Soc. Chim.* 1878, **29**, 9.

INDIUM. In. = 112·8.

314 This metal was discovered in Freiberg zinc-blende in the summer of the year 1863, by Reich and Richter, by means of spectrum analysis.[1] Indium also occurs as sulphide in other zinc-blendes, although present only in very small quantity. In order to prepare indium it is best to employ metallic zinc, such as that from Freiberg, which, however, does not contain more than 0·1 per cent. The metal is treated with such a quantity of hydrochloric acid that a small portion remains undissolved, and when the solution is allowed to stand for two or three days the whole of the indium is found to be precipitated on the residual zinc. The metallic powder is then washed off from the zinc, a few drops of dilute sulphuric acid added in order to dissolve any basic zinc chloride which may be formed, and the spongy metal well washed with hot water, then treated with nitric acid, and the acid solution, without filtration, boiled down with an excess of sulphuric acid until all the nitric acid is driven off. The solution is then filtered, the residue well washed, and a large excess of ammonia added to the filtrate. The zinc, cadmium, and copper then remain in solution whilst the whole of the indium together with iron, lead, and a small quantity of zinc, cadmium, and copper remains behind. After being well washed, the residue is dissolved in a small quantity of hydrochloric acid, an excess of hydrogen sodium sulphite added, and the solution boiled until it no longer smells of sulphur dioxide. A precipitate is thus obtained of basic indium sulphite, which for further purification may be dissolved in sulphurous acid ; on boiling this solution the pure salt separates out,[2] and this when strongly heated decomposes, leaving a residue of indium trioxide. The oxide can then be reduced to metal by ignition in a current of hydrogen or by fusion with sodium. The latter method appears to be the best suited for the preparation of large quantities. For this purpose the finely-divided oxide is placed in layers in a crucible with thin slices of sodium, the mixture pressed down and then covered with a thick layer of anhydrous sodium chloride. The porcelain crucible is next placed in a Hessian crucible provided with a cover and heated first gently and, as

[1] *J. Pr. Chem.* 1863, **89**, 444 ; **90**, 172 ; 1864, **92**, 480.
[2] Bayer, *Annalen*, 1871, **158**, 372.

soon as the reaction is over, to a moderate red-heat. The brittle alloy which is then obtained is boiled several times with water, washed with alcohol and ether, and again fused under a layer of potassium cyanide. The regulus is still not quite free from sodium, and in order to remove these traces it is thrown, in small pieces, into fused sodium carbonate, and the metal thus obtained in the pure state.[1]

Indium is a white non-crystalline metal, easily malleable and softer than lead. Its specific gravity is 7·42, and its melting point 176°. It retains its metallic lustre in the air, and even in boiling water. Heated on charcoal before the blow-pipe it colours the flame blue, and gives an incrustation of the oxide. It dissolves slowly in hydrochloric and dilute sulphuric acids, but readily in nitric acid.

Indium Oxide, In_2O_3, is a pale yellow powder, which on heating becomes brown, but regains its original colour on cooling. After ignition it dissolves only slowly in cold dilute acids, but quickly when the acid is warmed.

Indium Hydroxide, $In(OH)_3$, is formed when ammonia is added to a soluble indium salt. The hydroxide is thrown down as a gelatinous precipitate, which on boiling becomes heavy and dense, and when heated is easily converted into the oxide. It dissolves in caustic potash, but not in ammonia. When the oxide is heated in a current of hydrogen at 300°, a black pyrophoric powder is obtained, which appears to contain the lower oxide, InO.

SALTS OF INDIUM.

315 *Indium Trichloride*, $InCl_3$.—The metal burns at a dull red-heat in a current of chlorine, evolving a greenish-yellow light with formation of the chloride. The same compound is easily formed by heating the oxide, mixed with charcoal, in chlorine. It sublimes above 446° in the form of soft colourless plates, is extremely deliquescent, and dissolves in water with a hissing noise and evolution of heat. On evaporating the solution an insoluble basic salt is obtained. The vapour density of indium trichloride has been found by V. and C. Meyer[2] at a bright red-heat to be 7·87, corresponding to the formula $InCl_3$.

[1] Winkler, *J. Pr. Chem.* 1867, **102**, 273. [2] *Ber.* 1879, **12**, 611.

Indium Dichloride, $InCl_2$, is obtained as a white radiating crystalline mass by heating the metal in a current of hydrochloric acid. The vapour density of the dichloride has been shown by Nilson and Pettersson[1] to be 6·43 at 1300°, corresponding to the above formula. This compound is decomposed by water with fromation of the trichloride and separation of metallic indium:

$$3InCl_2 = 2InCl_3 + In.$$

Indium Monochloride, InCl, was prepared by the above-named chemists by distilling the vapour of the dichloride over the requisite amount of metallic indium; combination takes place, and the monochloride is obtained in the form of a mass resembling hæmatite which melts to form a blood-red liquid and can readily be vaporised. Its vapour density was found to be 5·5–5·3 at 1100–1400°. The monochloride undergoes a similar decomposition to the dichloride when brought into contact with water, the trichloride and metallic indium being formed:

$$3InCl = InCl_3 + 2In.$$

Indium also combines with bromine and iodine when heated in the vapours of these elements. The *tribromide* closely resembles the chloride, and the *tri-iodide* is a yellow crystalline mass, which on heating melts to form a reddish-brown liquid.

Indium Nitrate, $2In(NO_3)_3 + 9H_2O$, forms deliquescent needles soluble in both water and absolute alcohol. These on heating are easily converted into a basic salt.

Indium Sulphide, In_2S_3.—Indium and sulphur combine together at a temperature near redness, with evolution of heat, to form a brown infusible mass. Sulphuretted hydrogen passed into a solution of an indium salt which is not too acid or too concentrated, precipitates yellow indium sulphide, which on heating with sulphide of ammonium is converted into the white hydrosulphide.

Indium Sulphite, $In_2(SO_3),In_2O_3 + 8H_2O$.—This is a crystalline powder, the preparation of which has been already described. It dissolves easily in aqueous sulphurous acid, and separates out on evaporation in distinct crystals.

Indium Sulphate, $In_2(SO_4)_3$, is obtained by the careful evaporation of a solution of the trioxide in an excess of sulphuric acid,

[1] *Journ. Chem. Soc.* 1888, i. 814.

in the form of a white powder very soluble in water. On strongly heating it is converted into an insoluble basic salt. On evaporating the acid solution under the desiccator, deliquescent crystals of the acid salt having the composition $H_2In_2(SO_4)_4 + 8H_2O$ are deposited.

Indium-Ammonium Alum, $In_2(SO_4)_3 + (NH_4)_2SO_4 + 24H_2O$, is deposited in well-defined regular octohedra, which dissolve at 16° in half their weight, and at 30° in about a quarter of their weight of water and melt at 36°.[1] If a solution be allowed to crystallise at this temperature crystals of the hydrate $In_2(SO_4)_3 + (NH_4)_2SO_4 + 8H_2O$, separate out.

Potassium and sodium form analogous salts containing 8 molecules of water. The corresponding alums (containing 24 molecules of water) have not been obtained with indium and the fixed alkalis.

Detection and Estimation of Indium.

316 The indium compounds are distinguished inasmuch as when moistened with hydrochloric acid they tinge the non-luminous gas-flame a dark blue colour. The spectrum consists of an intense indigo-blue line, Inα w.l. 4511, and a less intense violet line, Inβ w.l. 4102. It is from the above reaction that the metal derives its name.

When heated on charcoal with sodium carbonate indium compounds yield white beads of the metal and a yellow incrustation of oxide. Zinc precipitates metallic indium from solutions of its salts. Caustic soda and potash precipitate the hydroxide, which partly dissolves in an excess, but is completely deposited again on boiling; it is insoluble in ammonia. This reaction is employed for the separation of indium from the other metals, as is also the formation of the insoluble basic sulphite, as has already been described, and the precipitation of a sulphide of indium which is insoluble in dilute acids.

The atomic weight of indium has been determined by Reich and Richter, as well as by Winkler[2] and Bunsen,[3] by converting the metal into the oxide. By dissolving in nitric acid and heating the nitrate, Winkler obtained the number 112·7, whilst Bunsen obtained the number 113. (O = 15·88.)

[1] Rössler, *J. Pr. Chem.* 1873 [2], **7**, 14.
[2] *Jahresb.* 1867, 260. [3] *Pogg. Ann.* 1870, **141**, 1.

THALLIUM, Tl = 202·6.

317 Thallium was discovered in the year 1861 by Crookes[1] in a seleniferous deposit obtained from a sulphuric acid manufactory at Tilkerode in the Harz. Selenium was being prepared from this deposit, and a considerable residue was left when the material was distilled. This was supposed at first to contain tellurium, but examination with the spectroscope showed that a new element was present whose spectrum consisted of one bright green line, whence the name of the element, from θάλλος, a green twig. In 1862 Lamy,[2] who discovered the element independently of Crookes, published the results of his investigations. It was first believed that this element was a non-metal belonging to the sulphur group, but it was afterwards found to be a metal, and was obtained in the metallic condition.

Thallium occurs in small quantities in many varieties of iron and copper pyrites, and in a few micas containing lithium. A mineral containing thallium has been discovered by Nordenskjöld[3] in a copper mine at Skrikerum, in Sweden. This mineral, to which he gave the name of crookesite, contains:—

Thallium . . .	17·25 per cent.
Selenium . . .	33·28 „
Copper	45·76 „
Silver	3·71 „
	100·00

The mineral water of Nauheim, near Frankfort, as well as that of many other mineral springs, contains small quantities of thallium.

For the purpose of preparing thallium it is best to employ the flue dust from sulphuric acid works, in which pyrites containing thallium is burnt. The dust, which contains selenium, arsenious oxide and small quantities of many other metals in the form of oxides or sulphates, is repeatedly boiled out with water acidulated with sulphuric acid, the solution concentrated and the

[1] "On the Existence of a new Element, probably of the Sulphur Group," *Chemical News*, **3**, 193 (March 30, 1861).

[2] *Société Impériale des Sciences de Lille*, May 2 and 16, 1862.

[3] *Annalen*, 1868, **145**, 127.

thallium precipitated with zinc, when it is deposited in the form of needles or glittering plates. Thallium may be obtained in a purer condition by boiling up the flue dust with water and adding hydrochloric acid to the concentrated clear solution. The precipitate is washed and gradually dissolved in half its weight of hot sulphuric acid, and then heated until all the hydrochloric and the greater part of the sulphuric acid has been driven off. The residue is next dissolved in water, the solution treated with sulphuretted hydrogen for the purpose of precipitating mercury, silver, arsenic, antimony, and bismuth, and ammonia then added to the filtrate to throw down any iron or alumina which may still be present. The filtrate, when concentrated, yields crystals of pure thallium sulphate, from which the metal may be obtained by deposition with zinc or by electrolysis. According to Bunsen[1] the solution of zinc sulphate obtained at the Juliushütte, at Goslar, contains 0·05 per cent. of thallium chloride, and if metallic zinc be allowed to remain in contact with the solution, copper, thallium, and cadmium are thrown down in the metallic state. The precipitated metals are then carefully washed with water and digested with dilute sulphuric acid to dissolve the last two metals. If potassium iodide be then added to this solution, thallium iodide separates out, and this on treatment with potassium cyanide yields pure metallic thallium.

It is stated that thallium occurs in almost all specimens of commercial platinum, sometimes to the extent of 0·1 per cent.[2]

Pure thallium has a bluish-white tint and a lead-like metallic lustre. It is crystalline, and so soft that it may be marked with the nail and leaves a streak on paper. It is malleable, but possesses little tenacity, and can only with difficulty be filed or sawn, as the particles stop up the interstices of the tool. Its specific gravity is 11·8; it melts at 290° (Lamy), volatilises at a very high temperature, and may be distilled in a current of hydrogen. Its vapour density[3] at 1728° is 14·25, corresponding to the molecular formula Tl_2. The density has not yet been determined at a series of different temperatures, so that this molecular formula can only be considered as a superior limit. When heated before the blow-pipe it oxidises, a pale reddish vapour being evolved which possesses a peculiar smell. It decomposes water at a red-heat and dissolves readily in nitric

[1] *Phil. Mag.* 1865 [4], **29**, 168.
[2] Warren, *Chem. News*, 1887, **55**, 241.
[3] Meyer and Biltz, *Ber.* 1889, **22**, 725.

and sulphuric acids, both dilute and concentrated, whilst it is less readily soluble in hydrochloric acid. Thallium readily forms alloys with other metals.

THALLIUM COMPOUNDS.

318 Thallium forms two distinct series of compounds, one of the type RX_3, corresponding to the position of the metal as a member of the aluminium group, the other of the type RX, closely analogous in many respects to the corresponding compounds of the alkali metals, but frequently bearing a strong physical resemblance to the corresponding compounds of lead.

Thallous Compounds.

Many of these compounds resemble the compounds of lead in their physical properties. Thus the halogen compounds (with the exception of the fluoride) are very sparingly soluble in water, and the sulphide is an insoluble black powder. On the other hand the hydroxide, the sulphate, and the carbonate are all soluble in water, and closely resemble the corresponding potassium salts; the sulphate, perchlorate, and phosphate, are moreover isomorphous with the corresponding salts of that metal.

Thallium Monoxide, Tl_2O.—When the metal is exposed to the air its surface assumes a dull grey colour, due to the formation of the above compound. This may be obtained in the pure state by heating the hydroxide in absence of air to a temperature of 100°. It is a black powder melting at about 300°, and easily dissolves in water with the formation of the hydroxide. Bromine converts it quantitatively into thallic oxide.

Thallium Hydroxide, Tl OH, is formed by the action of water upon the metal in presence of air. In order to prepare it in larger quantity a solution of the sulphate is precipitated with the necessary quantity of baryta water. It crystallises in long yellow needles having the formula $Tl\,OH + H_2O$. It is readily soluble in water, and the solution is colourless and possesses a strong alkaline reaction, turning yellow turmeric-paper brown. This brown colour disappears, however, after some time as the hydroxide destroys the colouring matter. Hence if turmeric-

paper be written upon with metallic thallium the writing at first appears brown but gradually disappears[1] (Erdmann).

Thallous Fluoride, Tl F, is formed by dissolving the carbonate in hydrofluoric acid. It crystallises in glittering octohedra and cube-octohedra. It dissolves in 1·25 parts of water at 15°, and less readily in boiling water. It melts on heating, and may readily be sublimed in a current of hydrofluoric acid.

Thallium Hydrogen Fluoride, $Tl HF_2$, is formed by allowing a solution of the fluoride in aqueous hydrofluoric acid to evaporate in a vacuum over sulphuric acid. It crystallises in similar forms to thallous fluoride, and dissolves in its own weight of water.

Thallium Monochloride, or *Thallous Chloride*, Tl Cl, is formed when the metal burns in chlorine, and separates out when hydrochloric acid is added to a tolerably concentrated solution of a soluble thallium salt, forming a white curdy precipitate which assumes a violet tint on exposure to light (Hebberling). It crystallises from hot saturated solutions in the form of cubes, and melts easily, yielding a yellowish liquid which on cooling solidifies to a white, shining, crystalline, somewhat flexible mass, having a specific gravity of 7·02 (Lamy) and boiling at 719–731.° Its vapour density has been found to be 8·5,[2] corresponding to the normal molecular weight. According to Hebberling 100 parts of water dissolve the following quantities of the salt:—

At	0°	16°	100°
Tl Cl	0·198	0·265	1·427.

It is less soluble in dilute hydrochloric acid, and hence the salt is precipitated from aqueous solution on addition of this acid. It is scarcely soluble in ammonia, and is insoluble in alcohol.

Thallous Bromide, Tl Br, is a very pale yellow precipitate, less soluble than the chloride, to which it possesses strong analogies. Bromine alone does not attack the metal so readily as chlorine, but in presence of water the metal is readily dissolved.

Thallous Iodide, Tl I, is formed when thallium and iodine are heated together. It may also be obtained by precipitating a solution of a thallium salt with potassium iodide, when it is thrown down as a beautiful yellow crystalline powder, which

[1] *J. Pr. Chem.* 1863, **89**, 381. [2] Roscoe, *Proc. Roy. Soc.* 1878, **27**, 426.

melts at 190°, yielding on solidification a red mass, which on standing becomes yellow. If it be precipitated from a hot solution containing potassium acetate it is deposited in the form of microscopic orange-yellow cubes or cube-octohedra (Werther). It is very sparingly soluble in cold water, 1 part requiring 16,000 parts for its solution, whereas it dissolves in 800 parts of boiling water. It is less soluble in a solution of potassium iodide, in alcohol, and in dilute acetic acid, than in water itself. It is not decomposed by dilute sulphuric acid, or hydrochloric acid, or caustic potash. Nitric acid, however, decomposes it with evolution of iodine.

Thallous Chlorate, $Tl\,Cl\,O_3$.—This salt is formed by mixing equivalent quantities of thallium sulphate and barium chlorate, filtering and concentrating the solution; the salt then separates out in microscopic prisms sparingly soluble in cold water (Thorpe).

Thallous Perchlorate, $Tl\,Cl\,O_4$, is formed by dissolving thallium in aqueous perchloric acid, or by precipitating barium perchlorate with thallium sulphate. It crystallises in transparent rhombic tables, isomorphous with potassium perchlorate, and having a specific gravity of 4·844 at 15°·5. One part of this salt dissolves at 15° in 10 parts, and at 100° in 0·06 parts of water; it is only slightly soluble in alcohol (Roscoe).

Thallium Monosulphide, or *Thallous Sulphide*, Tl_2S, is a black precipitate formed when sulphuretted hydrogen is passed into an alkaline or acetic acid solution of a thallous salt. If the solution contains a trace of free sulphuric acid, the sulphide separates out in the cold in microscopic tetrahedra (Hebberling). If the sulphide or a mixture of the metal with sulphur be melted in absence of air, a black glittering mass is obtained on cooling, having a specific gravity of about 8, and a general appearance somewhat like graphite. It is insoluble in water, alkalis, ammonium sulphide, and potassium cyanide. It dissolves with difficulty in acetic acid, but readily in mineral acids. The precipitated sulphide oxidises on exposure with formation of sulphate, and when heated in a current of hydrogen is reduced to thallium.

Normal Thallous Sulphate, Tl_2SO_4.—This salt crystallises in rhombic prisms isomorphous with potassium sulphate, and has a specific gravity of 6·6. 100 parts of water dissolve, according to Lamy, as follows:—

At	18°	62°	101°
Tl_2SO_4	4·8	11·5	19·3

Thallium sulphate melts at a red heat, decomposing in the presence of air with evolution of sulphur dioxide.

Thallous sulphate readily combines with other sulphates to form double salts such as $Tl_2SO_4 + MgSO_4 + 6H_2O$, isomorphous with the analogous potassium compounds. It can also replace the alkali sulphates in the alums. Thus thallium alum, $Tl_2SO_4 + Al_2(SO_4)_3 + 24H_2O$, crystallises in bright octohedra. Thallium iron alum and thallium chromium alum have also been prepared.

Hydrogen Thallous Sulphate, $HTlSO_4 + 3H_2O$, crystallises in short thick prisms, which melt on heating, and then suddenly decompose with evolution of vapours of sulphuric acid into the normal sulphate.

Thallous Nitrate, $TlNO_3$.—Nitric acid attacks thallium more easily than any other acid. Thallium nitrate crystallises in opaque, white rhombic prisms, having a specific gravity of 5·55. The crystals melt at 205°, and the fused mass solidifies on cooling to a glass-like solid. 100 parts of water dissolve, according to Lamy :—

At	18°	58°	107°
$TlNO_3$	10·67	43·48	588·2

It is insoluble in alcohol.

Phosphates of Thallium.—These salts are isomorphous with the analogous potassium compounds.

Normal Thallous Orthophosphate, Tl_3PO_4, is obtained in the form of needle-shaped crystals by precipitating the corresponding potassium salt with a thallium salt. It is also formed by the precipitation of ordinary sodium phosphate, but this precipitation is not complete (Lamy). One part dissolves at 15° in 201, and at 100° in 149 parts of water (Crookes). It is easily soluble in ammoniacal salts.

Monohydrogen Thallous Orthophosphate, $HTl_2PO_4 + H_2O$, is formed by neutralising a boiling solution of phosphoric acid with thallium carbonate. When evaporated to a syrup, the concentrated solution deposits rhombic crystals. These lose their water at 200°, and when they are heated to dull redness, a glassy mass of pyrophosphate remains behind.

Dihydrogen Thallous Orthophosphate, H_2TlPO_4.—This salt is obtained when phosphoric acid is added to a solution of the foregoing salt until the liquid exhibits a distinctly acid reaction. It crystallises in monosymmetric pearly tablets, dissolves readily

in water, and on ignition is converted into the glassy metaphosphate.

Normal Thallous Carbonate, Tl_2CO_3.—Thallium hydroxide readily absorbs carbon dioxide. Thus if the moistened metal be allowed to lie exposed to the air, it becomes covered with needle-shaped crystals of the carbonate. This salt crystallises from solution in water in glittering monosymmetric prisms, which have a caustic metallic taste and an alkaline reaction. 100 parts of water dissolve, according to Lamy:—

At	18°	62°	100°·8
Tl_2CO_3	5·23	12·85	22·40

It is insoluble in alcohol. It fuses on heating and decomposes at a higher temperature with evolution of carbon dioxide.

Hydrogen Thallous Carbonate appears not to be known in the solid state.

Thallous Cyanide, TlCN.—This salt is obtained by mixing strong solutions of potassium cyanide and thallium nitrate (Crookes). It separates in glittering plates not very soluble in water. When heated it decrepitates and melts easily, volatilising when strongly heated on platinum foil without reduction and without acting on the platinum. It is readily soluble in potassium cyanide and forms crystalline double cyanides.

Silicate of Thallium.—A solution of the hydroxide when boiled with amorphous silica dissolves this substance, and when the solution is evaporated a crystalline mass, having the composition $Tl_6Si_{10}O_{23} = 3\ Tl_2O + 10\ SiO_2$, and also containing water, separates out. When thallium oxide is fused with silica a yellow strongly refracting glass is obtained, which is occasionally employed in place of lead silicate for optical glass.

THALLIC COMPOUNDS.

319 Thallic oxide, like alumina, acts as a weak base. The salts with colourless acids are colourless and are as a rule readily decomposed when their solutions are heated, the hydrated oxide being deposited.

Thallium Trioxide, Tl_2O_3.—When molten thallium is plunged into oxygen-gas it takes fire with formation of this oxide. At a

red-heat this is, however, converted into the monoxide. It is also obtained by passing a galvanic current from a few Bunsen's elements through acidulated water, the positive pole consisting of metallic thallium which then becomes covered with a black deposit of this oxide[1] (Wöhler):

$$Tl_2 + 3H_2O = Tl_2O_3 + 3H_2.$$

If forms a dark reddish powder which is insoluble in water and the alkalis, and has the specific gravity 5·56.

Thallic Hydroxide, $Tl(OH)_3$.—If a hot solution of thallous chloride in sodium carbonate be mixed with one of sodium hypochlorite, a brown precipitate is obtained, which probably consists of amorphous thallic hydroxide, but on drying has the composition TlO(OH). The latter compound is also formed by the action of an alkali on thallic chloride. When treated with hydrochloric acid it evolves chlorine with formation of a thallous salt, whereas oxygen is given off when it is heated with concentrated sulphuric acid; on heating it is transformed into the trioxide and afterwards into the monoxide. If thallic oxide be fused for some time with potash containing a little water, thallic hydroxide, $Tl(OH)_3$, is left on treating the mass with water in the form of brown hexagonal plates, which are unaffected at a temperature of 340°.[2]

It was at one time supposed that thallic oxide was capable of uniting with strong bases to form thallates, as it was observed that when thallic hydroxide was suspended in caustic potash and a current of chlorine passed in, a deep reddish-violet solution was formed. It was, however, found that the coloration was caused by the presence of a trace of manganese in the thallic hydroxide employed.

Thallium Trichloride, or *Thallic Chloride*, $Tl\,Cl_3$, is formed when the monochloride is treated with chlorine under water. If the solution be evaporated in a vacuum, colourless deliquescent prisms having the composition $Tl\,Cl_3 + H_2O$ are deposited. When the metal or the monochloride is carefully heated in a current of chlorine, the compound $Tl\,Cl + Tl\,Cl_3$ is obtained, and this on further heating is transformed into $3Tl\,Cl + Tl\,Cl_3$, which is also formed as a yellowish-brown mass when metallic thallium is strongly heated in chlorine gas. This

[1] *Annalen*, 1868, **146**, 243, 375.

[2] Carnegie, *Chem. News*, 1889, **60**, 113.

substance is sparingly soluble in cold, but readily in hot water, separating from this solution in dark yellow six-sided tablets strongly resembling lead iodide in appearance. Ammonia decomposes it into the monochloride and the trioxide. When the metal is treated with nitrosyl chloride the compound $Tl\,Cl,Tl\,Cl_3,2NO\,Cl$ is formed. If an alcoholic solution of the trichloride be heated with alcoholic ammonia, a white crystalline precipitate of $(NH_3)_3Tl\,Cl_3$ separates out; this is decomposed on contact with water with formation of the violet-coloured trioxide :—

$$2(NH_3)_3Tl\,Cl_3 + 3H_2O = Tl_2O_3 + 6NH_4Cl.$$

The chloride also forms double salts with the chlorides of ammonium and potassium.

Thallium Trisulphide, or *Thallic Sulphide*, Tl_2S_3, is formed when the metal is fused with an excess of sulphur. It is a black amorphous mass, which at a summer temperature is soft and plastic like pitch. Below 12° it is hard and brittle, exhibiting a glassy fracture.

If 1 part of thallium sulphate be fused with 6 parts of sulphur and 6 parts of potassium carbonate, and the mass treated with water, a red crystalline powder remains behind having the composition $KTl\,S_2$. This substance is not attacked by caustic potash, but decomposes in presence of acids.

Thallic Sulphate, $Tl_2(SO_4)_3 + 7H_2O$, crystallises on evaporation of a solution of the trioxide in warm dilute sulphuric acid in the form of thin colourless tablets, which are decomposed by water with separation of the hydrated trioxide.

No true alums have as yet been prepared containing thallic sulphate in place of aluminium sulphate. The compound Tl_2SO_4, $Tl_2(SO_4)_3$ is formed when equivalent amounts of thallous and thallic sulphate are dissolved in water and the solution allowed to crystallise. The salt is anhydrous but crystallises in cubes and octohedra.[1]

Thallic Nitrate, $Tl(NO_3)_3 + 8H_2O$, is deposited from a solution of the oxide in nitric acid in colourless crystals, which decompose on heating with water.

[1] Lepsius, *Chem. Central.* 1891, i. 694.

Detection and Estimation of Thallium.

320 The salts of thallium are poisonous. The soluble salts possess a disagreeable metallic taste. Their presence may be readily detected by the beautiful green colour which they impart to a non-luminous gas-flame. The spectrum of this flame consists of one bright green line having a wave-length of 5351, not coincident with any line in the solar spectrum. Thallium may be readily separated from all the other metals by treating an acid solution with sulphuretted hydrogen, filtering off the separated sulphides, and precipitating the filtrate with sulphide of ammonium, which throws down thallium sulphide as a black precipitate. This precipitate may also contain the sulphides and hydroxides of the metals of the iron group; to separate these, it is washed, dissolved in nitric acid, and the boiling solution neutralised with sodium carbonate; on cooling, chloroplatinic acid is added, when a pale yellow precipitate of the double chloride of thallium and platinum, $2\ Tl\ Cl + PtCl_4$ is thrown down. This compound dissolves in 15,600 parts of cold water, and hence may be employed for the quantitative determination of thallium. Thallium may also be precipitated by potassium iodide as thallium iodide, which in presence of an alkali iodide is altogether insoluble in water.

The Atomic Weight of Thallium has been determined by Crookes[1] by converting the metal into the nitrate. Ten experiments gave numbers lying between 202·62 and 202·65. (O = 15·88.)

The number 202·6 has been confirmed by Lepierre who analysed thallic oxide and thallous sulphate, and determined the amount of thallic oxide which could be obtained from a thallous salt.[2]

[1] *Phil. Trans.* 1873, 277. [2] *Compt. Rend.* 1893, **116**, 580.

METALS OF THE RARE EARTHS.

Scandium	(Cerium)	Decipium
Yttrium	Erbium	Dysprosium
Lanthanum	Gadolinium	Holmium
	Praseodymium	Neodymium
	Samarium	Terbium
	Ytterbium	Thulium

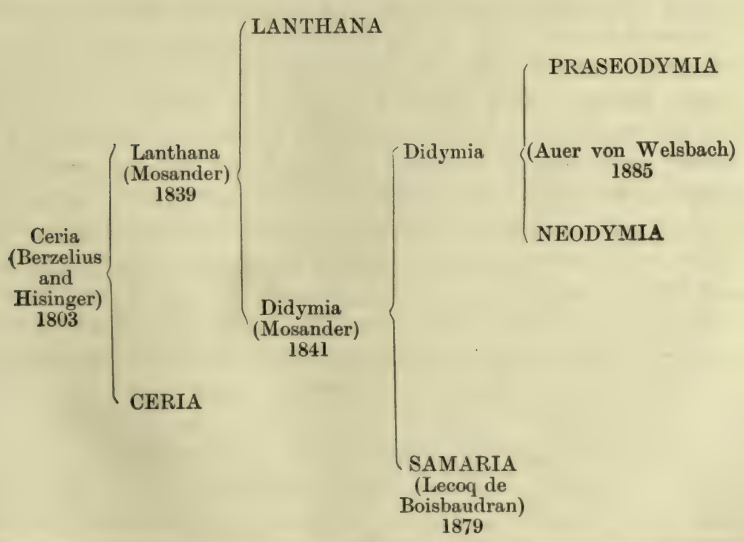
321 The three metals of the boron group are also members of the very extensive class of elements known as the metals of the rare earths. The names of these are given above in three groups, the first of which comprises the three metals which with boron make up sub-group *a* of group III.; the second, those of which the individuality is at least possible; the third, those which are probably mixtures of greater or less complexity. Cerium, although closely related to the others in chemical behaviour, belongs to group IV. and is described along with the metals of that group. So little is known of the chemical relationships of the remaining metals that they cannot at present be included in the periodic system, and are therefore described along with scandium, yttrium and lanthanum, with which they occur and which they closely resemble in properties.

The earths formerly described as philippia and mosandria have been proved to be mixtures of other earths.

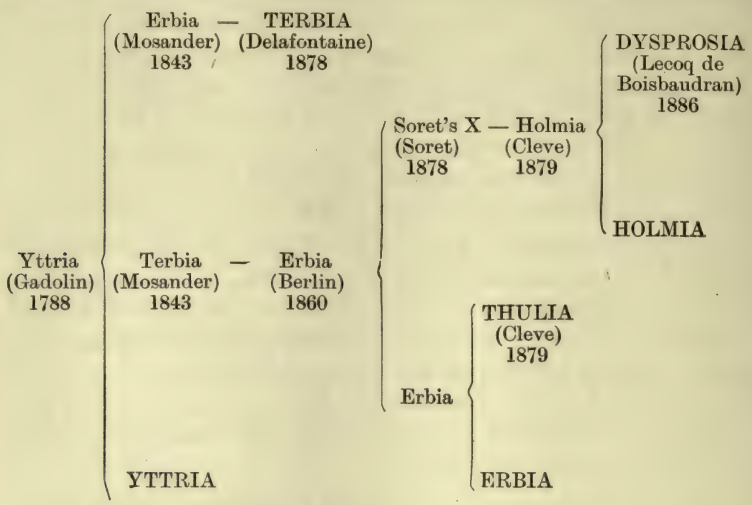
322 In the year 1794 Professor Gadolin of Abo in Finland discovered a new earth in the mineral, termed after him gadolinite, which had been found at Ytterby in the year 1788. This discovery was confirmed in the year 1797 by Eckeberg, who found that the compound separated by Gadolin contained, together with glucina, a new earth, to which he gave the name of yttria. In 1803 Klaproth discovered a second peculiar earth in another Swedish mineral found at Riddarhyttan, which mineral had formerly been supposed to contain tungsten, and to this, because it became dark-yellow on heating, he gave the name of ochroite. The same substance was examined simultaneously by Berzelius and Hisinger, who considered it as the oxide of a new metal which they termed cerium, after the planet Ceres, which had been recently discovered, whilst the mineral was called cerite.

In 1819 Berzelius observed that crude yttria also contained ceria; and Mosander, in 1839, showed, in a most careful investigation, that ceria contained the oxide of another metal, to which he gave the name of lanthanum (λανθάνω, I lie hidden); and in 1841 he discovered that the latter was not pure, but contained a third new element, to which he gave the name didymium (from διδύμοι, twins). The same chemist in 1843 concluded from another series of investigations that yttrium was invariably accompanied by two other metals, to which he gave the names of terbium and erbium from the terminal letters of the stem of the word Ytterby. According to the investigations of Bunsen and Bahr,[1] only one of the last two metals appeared to exist, and for this they retained the name erbium but the subsequent researches of Delafontaine and Marignac showed that both elements were present.

Further investigations have proved that the substances which these chemists examined were in most cases highly complex mixtures, the complete separation of which has not yet been effected. This is illustrated by the two following tables which show the earths which have so far been obtained from yttria and ceria. The name of the investigator who effected each separation is added together with the date. Further details will be found under the headings of the separate metals.



[1] *Annalen*, 1866, **137**, 1.



323 The rare earths occur in several rare minerals found in various localities in Scandinavia, Siberia, Greenland and North America. They are usually present in the form of silicates, less frequently as niobates, tantalates, phosphates, fluorides and uranates, and are often accompanied by the oxides of beryllium and zirconium. The most important of these minerals are *gadolinite*, a basic orthosilicate of beryllium, iron and the yttrium metals; *cerite*, a hydrated silicate of calcium and the cerium metals (didymium, lanthanum, &c.); *keilhauite*, a titanosilicate of yttrium, aluminium iron and calcium; *samarskite*, a niobate and tantalate of iron, calcium, uranyl and the metals of both the cerium and yttrium groups; *fergusonite*, a niobate of yttrium, erbium and cerium; and *euxenite*, a niobate and titanate of yttrium, cerium, erbium and uranyl. The subjoined analyses[1] give some idea of the general composition of three of these minerals.

The crude earths are obtained from the minerals by methods which differ somewhat according to the nature of the material to be treated. Cerite is evaporated with strong sulphuric acid, the excess of acid removed by heating and the residue dissolved in ice-cold water. The clear solution is saturated with sulphuretted hydrogen, again filtered, and then made acid with hydrochloric acid and precipitated with oxalic acid, by means of which the insoluble oxalates of the earths, consisting mainly of ceria, lanthana and didymia are obtained and are finally converted into the oxides by ignition. Gadolinite, on the other

[1] Quoted from Dana's *Mineralogy* (1892).

Cerite. (Lindström, 1873.)		Gadolinite from Ytterby. (Petersson, 1890.)		Samarskite from N. Carolina. (Allen, 1877.)	
SiO_2	22·79	SiO_2	23·88	Ta_2O_5	18·20
Ce_2O_3	24·06	ThO_2	0·41	Nb_2O_5	37·50
Di_2O_3, La_2O_3	35·37	Y_2O_3	45·30	SnO_2, WO_2	0·08
		Ce_2O_3	3·84		
FeO	3·92	Di_2O_3, La_2O_3	2·57	UO_3	12·54
Al_2O_3	1·26			Ce_2O_3, Di_2O_3, La_2O_3	4·17
CaO	4·35	Fe_2O_3	0·60		
H_2O	3·44	FeO	12·89	Y_2O_3	14·48
Gangue	4·33	BeO	9·91	FeO	10·75
		CaO, MgO	0·54	MnO	0·78
		Na_2O	0·15	CaO	0·55
		H_2O	0·57	H_2O	1·12
	99·52		100·66		100·17

hand, is decomposed by hydrochloric acid, and the oxalates then precipitated from the solution of the chlorides. In other cases (fergusonite), the mineral is fused with potassium bisulphate, the fused mass extracted with water and then the earths precipitated as hydrates or oxalates.

The nature of the crude oxide thus obtained varies very greatly according to the source from which it is derived. The different earths, with but few exceptions, resemble one another very closely, so that, in order to separate them, advantage has to be taken of very slight differences in chemical behaviour and the processes of separation repeated a very large number, often amounting to many hundreds, of times. It is therefore advisable to commence the preparation of any particular earth with a mineral which contains it in as large a proportion and as free from admixture as possible, since in this way the length and tediousness of the processes of separation are lessened.

A rough division of the mixed earths into two groups is obtained by saturating the neutral solution of the crude oxide in nitric acid with potassium sulphate. Double salts are formed of the general formula $R_2(SO_4)_3,3K_2SO_4$, those of the yttrium group (Y, Yb, Er, Ho, Tm, Tr, Sc) being soluble whilst

those of the cerium group (Di, La, Ce, Sm, Dp, Gd) are insoluble in a saturated solution of potassium sulphate. The sulphates thus obtained may be reconverted into oxalates or oxides and the separation repeated as often as is desired. Cerium may then be removed by converting the oxides into sulphates and boiling with water, under which circumstances a basic sulphate is precipitated. For the further separation of the oxides which have been submitted to the foregoing treatment a number of different methods has been proposed, two of the most important of which alone are here given.[1]

(1) *Ignition of the nitrates* (Bahr and Bunsen). When the neutral nitrates of the earths of either of these groups are gently heated, it is found that the salts of the different earths are decomposed at different temperatures. In the case of the yttrium group of oxides, to which the method is best applied, the nitrates decompose in the following order, Sc, Yb, Er, Ho, Tm, Tr, Y; yttrium nitrate requiring the highest temperature. The heating is therefore only continued until a slight amount of decomposition has taken place; the cooled mass is then extracted with boiling water and the basic salt which separates on cooling removed by filtration. The filtrate is then evaporated and the process repeated.

(2) *Fractional precipitation with ammonia or some other base.* The neutral nitrate obtained from the crude earth is dissolved in water and ammonia added in such quantity as only to precipitate a portion of the earths which are present, the solution being so dilute that the precipitation takes place slowly. In this way the least basic earths are first precipitated whilst the most basic are found in the filtrate. Among the cerium group of earths, lanthana appears to be the most basic, and is followed by didymia, samaria, gadolinia, and decipia. The precipitated hydrate is filtered off, redissolved in nitric acid, and again submitted to fractional precipitation, whilst the filtrate is treated in a similar manner to the original solution. Very valuable results have been obtained by using aniline in conjunction with ammonia. For this purpose the earths are dissolved in hydrochloric acid, an excess of aniline added and finally an amount of ammonia insufficent to completely precipitate the earths present. That portion of the least basic earths which is least readily soluble in aniline hydrochloride is thus precipitated, the more readily soluble portion being left in solution.

[1] Compare Losse, *Zeit. Anorg. Chem.* 1892 **3**, 56.

In addition to these methods many systems of fractional crystallisation of salts, such as the formates, nitrates and oxalates, and other modes of separation, have been adopted by various chemists.

324 The progress of the separation effected by any of these means may be followed by several methods, one of the most reliable of which is the determination of the chemical equivalent of the oxide obtained. This is accomplished by precipitating the earth in the form of oxalate, igniting, and weighing the oxide, which is then exposed to steam and afterwards evaporated with dilute sulphuric acid and heated gently over a small flame until the weight is constant. The amount of sulphate formed from a known weight of oxide is thus ascertained, from which the equivalent of the earth can be calculated. This method is of great value when the earths which are being separated differ considerably in their equivalents, but is, of course, less useful when, as is often the case, the mixture consists of earths which have nearly the same equivalent.

The other methods employed for detecting the progress of purification or separation are all applications of spectrum analysis. In addition to the spark spectra, or those shown in the electric arc, the salts of many of the earths in solution exhibit characteristic absorption spectra. A number of the earths, moreover, show "phosphorescence spectra" when the ignited earth or its basic sulphate is exposed to an electric discharge in a highly exhausted glass bulb (Crookes), or exhibit a characteristic spectrum when an induction spark is made to pass from a positive pole of platinum on to the centre of the surface of a solution of one of the salts of the earth, which is connected with the negative pole (reversion spectra of Lecoq de Boisbaudran).

The evidence afforded by the study of the spectra yielded by the earths in any of these ways cannot be accepted as quite conclusive, because we are at present unacquainted with the exact influence of many variable conditions, especially the presence of other substances, upon the phenomena in question. Such evidence as has been gathered, however, all points in one direction, viz., to the probability that most of the earths which have been described are not chemical individuals, but mixtures, in many cases of great complexity, which have not yet been unravelled. Thus Krüss and Nilson, examining the absorption spectra of the nitrates of the earths obtained from different

sources, found that these differed in many cases by the absence or altered intensity of some of the absorption bands. From this they concluded, to take a single instance, that the spectrum which had previously been ascribed to didymia and which was given by salts of didymium was really composite and due to a number of distinct substances known in the aggregate as didymia, the absence of some of which from the minerals examined gave rise to the incomplete spectra which were observed. They concluded from a long series of researches [1] that the minerals examined by them contained at least 24 elements of this group, the salts of which give absorption spectra. Crookes has arrived at similar conclusions from a study of the phosphorescence spectra, about 30 different elements being, according to him, contained in the substances known to us as the rare earths. Yttria, for example, when submitted to repeated fractional precipitation by ammonia yields a less basic and a more basic fraction, the phosphorescence spectra of which differ completely from each other and are much simpler than that of the original earth, consisting of three and four respectively out of the ten bands contained in the original spectrum.[2]

The chemical evidence, as far as it has been obtained, tends to support the conclusions drawn from the spectroscopic investigations. Krüss, for instance, submitted the substances known as erbia, holmia and terbia to fractionation by means of various reagents, including ammonia and aniline, and did not succeed in obtaining from any one of these an earth of constant equivalent and incapable of being split up into substances of different equivalent by further treatment.

Under these circumstances the derivatives of only a few of the better known earths will be here described in detail.

325 The metals of this group were at first supposed to be divalent, the general formula of the earths being written RO. In 1870, Mendeléeff found that whilst the equivalent of cerium was 46·3, its specific heat was about 0·05, whilst Hillebrand obtained the more accurate number 0·04479. According to this the atomic weight of cerium must be 139 and not 92·6 as previously supposed, since $139 \times 0{\cdot}04479 = 6{\cdot}3$, the lower basic oxide being therefore Ce_2O_3 and the higher oxide CeO_2.

It was suggested at the same time that the basic oxides of didymium and lanthanum, which had nearly the same equivalent as cerium, might be Di_2O_3 and LaO_2, didymium (138) being

[1] *Ber.* 1887, **20**, 2170. [2] *Journ. Chem. Soc.* 1889, i. 250.

placed in the third group of the periodic system, and lanthanum, with an atomic weight of about 180, in the fourth group along with cerium. In this way these metals found a place in the periodic system, whilst no place exists for them in that system if their atomic weights be taken as about 92. The atomic weight of yttrium, the compounds of which were then but little known, was at the same time altered for similar reasons from about 59 to 88, the oxide being formulated Y_2O_3 instead of YO, and the metal placed in the third group of the periodic system.

The subsequent determination of the specific heats of lanthanum (0·04485) and didymium (·04563) by Hillebrand showed that both these metals had an atomic weight of about 140, and a more accurate determination of their equivalents led to the atomic values La = 137·5, Di = 144. Oxide of lanthanum was, therefore, formulated La_2O_3 and the metal placed in the third group. The salts of didymium have since that date been shown to consist of the salts of at least two distinct elements, and the relations of these to the other elements have not yet been satisfactorily decided.

At present the general formula R_2O_3 is applied to the basic oxides of all the rare earth metals, and the formulæ of their salts written in accordance with this.

The oxides of many of the rare earths, along with those of zirconium and thorium are employed in the incandescent gas lamps introduced by Auer v. Welsbach. A mantle of some fibrous material is saturated with a solution of the salts of these earths, dried and ignited. The oxides thus produced glow with a brilliant light when heated in a non-luminous gas flame, the colour of the light depending on the nature of the oxides.

SCANDIUM. Sc = 43·8.

326 The oxide of this metal, which has not itself been isolated was discovered by Nilson in euxenite in 1879.[1]

Scandium occupies the place in the periodic system which was assigned by Mendeléeff in 1869 to the unknown element ekaboron (p. 61). Speaking of this undiscovered element he said in the course of a full discussion of the subject[2]: Its atomic

[1] *Ber.* 1879, **12**, 554; 1880, **13**, 1439.

[2] *Annalen Supplementband*, 1872, **8**, 197.

weight will be about 44, and its oxide, Ek_2O_3, will be a stronger base than alumina and will have a specific gravity of about 3·5, whilst the specific gravity of the chloride will be about 2. The oxide will be insoluble in alkalis and the salts colourless, yielding gelatinous precipitates with potash, potassium carbonate, sodium phosphate, &c.

Scandium hydroxide, $Sc(OH)_3$, is a gelatinous white precipitate which on ignition yields the *oxide*, Sc_2O_3. The latter is a white powder resembling magnesia, of specific gravity 3·864. The salts are colourless and exhibit no absorption bands. The double sulphate of scandium and potassium, $Sc_2(SO_4)_3,3K_2SO_4$ is insoluble in a solution of potassium sulphate. The spark spectrum of the chloride is characteristic (Thalén).

YTTRIUM. Y=88

327 Cleve obtained yttrium as a dark grey powder possessing a metallic lustre under the burnisher. He prepared it by the electrolysis of the double chloride of yttrium and sodium, and also by fusing this salt with sodium. Yttrium decomposes water slowly in the cold but more quickly on boiling.[1]

Yttrium Oxide, Y_2O_3, is obtained as a white powder by igniting the oxalate or hydroxide. On ignition this emits a bright white light. It does not combine directly with water, but when a yttrium salt is precipitated with an alkali the hydroxide is thrown down as a gelatinous precipitate. Yttrium oxide dissolves slowly but completely in hydrochloric, nitric, and sulphuric acids. According to Crookes it is a complicated mixture.[2]

Yttrium Fluoride occurs together with the fluorides of cerium and calcium in the mineral yttrocerite found near Fahlun in Sweden, at Amity, Orange County, New York, in Massachusetts, and at Mount Mica in Maine. It is massive, crystalline-granular and earthy, having a glistening vitreous to pearly lustre, and a colour varying from violet-blue to grey and white. Sometimes it has a reddish-brown colour.

Yttrium Chloride, YCl_3, formed by heating the oxide mixed with carbon in chlorine, is a white non-volatile body. When

[1] Cleve, *Compt. Rend.* 1882, **95**, 1125.
[2] *Journ. Chem. Soc.* 1889, i. 250.

the oxide is dissolved in hydrochloric acid the hydrate $YCl_3 + 6H_2O$ is obtained on evaporation in deliquescent prisms which are soluble in alcohol but insoluble in ether. These decompose when heated alone with evolution of hydrochloric acid; but when ignited in presence of sal-ammoniac the anhydrous chloride is obtained.

The bromide and iodide are very similar to the chloride.

Yttrium Sulphide, Y_2S_3, is obtained as a yellow or grey powder by heating the oxide in the vapour of carbon bisulphide (Popp) and by heating the chloride in sulphuretted hydrogen. It is not soluble in water, but is decomposed by acids (Wöhler).

Yttrium Sulphate, $Y_2(SO_4)_3 + 8H_2O$, forms transparent crystals which lose their water at 115°. 100 parts of cold water dissolve 9·3 parts of salt, but when the solution is warmed to 100°, 4·5 parts separate out in the crystalline state.

Yttrium Nitrate, $Y(NO_3)_3 + 6H_2O$, is easily soluble in water, alcohol, and ether, forming large needles.

Yttrium Orthophosphate, $YPO_4 + 2H_2O$, is slightly soluble in water; the *metaphosphate*, $Y(PO_3)_3$, is an insoluble crystalline powder; and the *pyrophosphate*, $2YHP_2O_7 + 7H_2O$, is soluble in water.

Yttrium Carbonate, $Y_2(CO_3)_3 + 3H_2O$, is a heavy white powder insoluble in water.

Detection and Estimation of Yttrium.

328 This metal is most readily recognised by the spark spectrum of the chloride. This contains a large number of bright lines, of which two groups lying near the sodium line towards the red are especially characteristic. The salts show no absorption spectrum. The reactions of the yttrium salts are very similar to those of zirconium.

The *atomic weight* of yttrium was determined by Bahr and Bunsen by the analysis of the sulphate to be 92. According to Cleve and Hoeglund[1] on the other hand it is 89·2. This difference is probably due to the presence of other earths. From a still later determination[2] Cleve obtained the number 88·4.

[1] *Bull. Soc. Chim.* 1872 [2], **18**, 193.
[2] *Bull. Soc. Chim.* 1883 [2], **39**, 120.

LANTHANUM. La = 137·5

329 Mosander obtained metallic lanthanum as a grey powder by heating the chloride with potassium. Hillebrand and Norton[1] prepared it by the electrolysis of the fused chloride, and obtained it in the form of fused globules, some of which weighed as much as six grams. Thus prepared it has a specific gravity of 6·163 and an iron grey colour; it takes a high polish, but soon tarnishes, even on exposure to dry air, attaining a steel-blue colour. The metal can be hammered out to tolerably thin foil, but cannot be drawn into wire. The specific heat of the metal is 0·04485. The finely-divided metal burns brightly when thrown into the flame. It also takes fire when thrown into chlorine gas, burns less brightly in bromine vapour, and combines with iodine without evolution of light. Cold water oxidises it slowly with formation of the hydroxide. Cold concentrated sulphuric acid does not attack it, but in dilute sulphuric acid and in hydrochloric acid it dissolves with violent evolution of hydrogen gas, and is oxidised both by concentrated and dilute nitric acid.

Lanthanum Oxide, La_2O_3.—This is obtained in the form of a white powder, which has a specific gravity of 6·48, by heating the hydroxide, oxalate, carbonate, or nitrate. It combines with water with evolution of heat, like lime, with formation of a voluminous snow-white powder of *lathanum hydroxide*, $La(OH)_3$, which is also obtained by precipitating a lanthanum salt with an alkali in the form of a gelatinous precipitate which easily absorbs carbon dioxide from the air. The hydroxide has an alkaline reaction and decomposes ammonium salts on heating.

The oxide is readily reduced when it is heated with magnesium powder. If the reaction be carried out in an atmosphere of hydrogen, a *hydride of lanthanum* is formed which has not yet been obtained pure.[2]

Lanthanum Chloride, $LaCl_3$.—This body is obtained in the anhydrous state by heating its ammonium double salt. It is a crystalline mass very soluble in water and alcohol. When the oxide is dissolved in hydrochloric acid, and the solution evaporated to a syrup, large prisms having the composition

[1] *Pogg. Ann.* 1875, **156**, 466.

[2] Winkler, *Ber.* 1890, **23**, 787; 1891, **24**, 890.

$2LaCl_3 + 15H_2O$ are deposited, and these when heated lose hydrochloric acid.

Lanthanum Sulphide, La_2S_3, is obtained by heating the oxide in the vapour of carbon bisulphide, in the form of a yellow mass which is decomposed by water.

Lanthanum Sulphate, $La_2(SO_4)_3 + 9H_2O$, crystallises in six-sided pointed prisms which are more soluble in cold than in hot water. One part of the anhydrous salt dissolves at 3° in less than 6 parts, whilst at 100° it dissolves in about 115 parts of water. The double potassium salt is insoluble in a solution of potassium sulphate.

Lanthanum Nitrate, $La(NO_3)_3 + 6H_2O$, is a salt easily soluble in water and alcohol, crystallising in oblique prisms or tables.

Lanthanum Carbide, LaC_2 is formed when a mixture of the oxide with sugar charcoal is heated in the electric furnace. It is a crystalline substance and is readily attacked by acids. Water decomposes it with evolution of a mixture of acetylene, methane, a very small amount of ethylene and traces of liquid and solid hydrocarbons.[1]

Lanthanum Carbonate, $La_2(CO_3)_3 + 8H_2O$.—This occurs as lanthanite, a mineral which contains varying quantities of cerium and crystallises in greyish-white, pink, or yellowish rhombic prisms. It occurs at Bastnäs in Sweden; also in Silurian limestone with the zinc ores of the Saucon Valley, Lehigh County Pa., and in other localities in the United States. When a lanthanum salt is precipitated with a soluble carbonate, this same salt is obtained in the form of glittering scales.

Detection and Estimation of Lanthanum.

330 Lanthanum chloride yields a spectrum consisting of many very bright and characteristic lines, by means of which even traces of the metal can be readily detected. The salts of lanthanum possess an astringent sweet taste. They do not show an absorption spectrum.

Lanthanum is determined quantitatively by precipitating it either as hydroxide or as oxalate, these being converted by ignition into the oxide.

The atomic weight of lanthanum has been obtained at various times by many chemists but with varying results. The most

[1] Moissan, *Compt. Rend.* 1896, **123**, 148.

recent experiments, however, yield fairly concordant numbers. Thus Cleve [1] found the atomic weight to be 137·3, Bettendorf [2] 137·6 and Brauner [3] 137·6.

DIDYMIUM.

Praseodymium, Pr = 142·5. Neodymium, Nd = 139·7

331 The substance originally described as didymia by Mosander (p. 623) was found by Lecoq de Boisbaudran in 1879 to contain the oxide of another element, named by him samarium, from which it was separated by repeated fractional precipitation with ammonia. Didymia, freed from samaria, was then looked on as an individual substance until in 1885 Welsbach [4] succeeded in resolving it into the oxides of two distinct elements, which he termed praseodymium and neodymium. This was accomplished by the oft repeated fractional crystallisation, from a strong nitric acid solution, of the double nitrate of the metal with ammonium, or, in the last stage of the process, sodium nitrate.

As the separation is exceedingly difficult to effect, a short account of the derivatives hitherto known as those of didymium is given.

Marignac was the first to prepare metallic didymium by heating the chloride with potassium. He obtained the metal in the form of a green powder or in very small globules. Hillebrand and Norton obtained it in larger quantity by the electrolysis of the fused chloride. It possesses a slightly yellow tint and tarnishes with a yellow colour on exposure to the air; the filings of the metal burn with a splendid bright light when held in the flame. Didymium has a specific gravity of 6·544. It forms two oxides, Di_2O_3 and Di_2O_5.

Didymium Trioxide, Di_2O_3, is formed by igniting the hydroxide or a salt containing a volatile acid. It is a dirty-blue mass having a specific gravity of 6·950. The *hydroxide*, $Di(OH)_3$, is a slightly rose-red precipitate, which on drying has a reddish-grey colour. Both compounds decompose ammoniacal salts on heating.

[1] *Bull. Soc. Chim.* 1883 [2], **39**, 151.
[2] *Annalen*, 1890, **256**, 159.
[3] Brauner, *Monatsh.* 1882, **3**, 493.
[4] *Monatsh.* 1885, **6**, 477.

Didymium Pentoxide, Di_2O_5, has been prepared as a brown powder by Brauner [1] by heating the nitrate in oxygen.

Didymium Chloride, $DiCl_3 + 6H_2O$, forms rose-red monosymmetric crystals, which are easily soluble in water and which decompose on heating. When the solution of the salt mixed with sal-ammoniac is evaporated to dryness and the residue ignited in absence of air, the anhydrous salt is obtained as a fibrous crystalline rose-red mass.

Didymium Bromide, $DiBr_3 + 6H_2O$, crystallises in violet prisms, which do not deliquesce on exposure to the air.

Didymium Sulphide, Di_2S_3, is obtained as a greenish-brown powder by the ignition of the oxide in the vapour of carbon bisulphide. It is slowly decomposed by water and quickly by dilute acids.

Didymium Sulphate, $Di_2(SO_4)_3 + 8H_2O$, crystallises readily in large rose-red lustrous six-sided prisms, which completely lose their water of crystallisation at 200°. When the cold concentrated solution is boiled, $Di_2(SO_4)_3 + 9H_2O$, separates out. It is insoluble in a solution of potassium sulphate.

Didymium Nitrate, $Di_2(NO_3)_3 + 6H_2O$, forms large violet crystals which are very easily soluble in water and alcohol. The concentrated solution has a violet colour, and when diluted it assumes a rose-red tint.

Didymium Carbonate, $Di_2(CO_3)_3$, is a red crystalline powder obtained by passing carbon dioxide through water containing the hydroxide in suspension.

332 *Praseodymium* forms two oxides. The *sesquioxide*, Pr_2O_3, is obtained by the reduction of the higher oxide as a greenish-white mass soluble in dilute acids. The *peroxide*, Pr_4O_7 is very readily formed when the sesquioxide is heated in the air and is a lustrous black-brown mass, which dissolves in sulphuric acid with evolution of oxygen.

The salts are green and form brilliant green solutions, the absorption spectrum of which shows only a few of the bands characteristic of didymium. The oxide does not yield a discontinuous emission spectrum, but gives a characteristic spark spectrum.

Neodymium only forms one *oxide*, Nd_2O_3, which is of a faint blue colour. The salts have a splendid amethyst colour and form pink solutions. The absorption spectrum of the neodymium salts contains all, except one, of those bands of the

[1] *Journ. Chem. Soc.* 1882, i. 68.

original didymium spectrum, which are wanting in the absorption spectrum of the salts of praseodymium.

The oxide has a characteristic emission spectrum which is identical with that of the original didymia, and also gives a complex spark spectrum. It seems probable that neodymia is not entirely free from other, hitherto unknown, earths.

The "didymium" salts appear to contain a larger proportion of neodymium than of praseodymium. These salts can be reproduced with their original colour by mixing the salts of these two elements in the proper relative amounts.

GADOLINIUM. Gd = 155

333 This element was discovered in 1880 by Marignac in samarskite.[1] The oxide, Gd_2O_3, is white and the salts are colourless and do not show absorption bands.

TERBIUM. Tr = 162

334 The existence of the earth originally called erbia by Mosander, was denied by Berlin (1860), and by Bahr and Bunsen (1866) but was confirmed by Delafontaine (1878) and Marignac. It then received the name of terbia, the designation erbia having been in the meanwhile applied to the rose-red earth described below. It forms a dark orange-coloured oxide, whilst its salts are colourless and show no absorption bands.

It is very doubtful whether terbia is a pure substance.[2]

ERBIUM. Er = 165

335 The terbia originally isolated from crude yttria by Mosander subsequently received the name of *erbia* (Berlin), and has been shown by Soret, Cleve, Thalén and Lecoq de Boisbaudran, to consist of at least four earths, the true *erbia*, *holmia*, *thulia* and *dysprosia*. The salts of all these show absorption bands, but it is doubtful whether any one of the four is an individual substance.[3] Erbium forms a rose coloured oxide and salts of the same colour, which in solution show absorption bands.

[1] *Ann. Chim. Phys.* 1880 [5], **20**, 535.
[2] Krüss, *Zeit. Anorg. Chem.* 1893, **4**, 26.
[3] Compare *Zeit. Anorg. Chem.* 1892, **3**, 353, 407.

YTTERBIUM. Yb = 172

336 This element was discovered by Marignac in gadolinite in 1878.[1] It forms one *oxide*, Yb_2O_3, which is white; its salts are colourless and yield no absorption bands, but the spark spectrum is characteristic (Thalén). The double sulphate is soluble in potassium sulphate solution.

SAMARIUM Sm = 149

337 This metal was discovered in samarskite by Lecoq de Boisbaudran. The oxide is white whereas the salts are topaz-yellow and show absorption bands. It yields a characteristic spark spectrum.

DECIPIUM. Dp = 170

338 In 1878 Delafontaine isolated from samarskite an earth which he called decipia, but which was afterwards found to contain samaria. When free from the latter the salts are colourless and without absorption bands.[2]

The existence of a number of other earths has been surmised, as already mentioned, from a study of the spectra given by the various substances of this class, but these have not as yet been isolated from the complex mixtures in which they are supposed to occur.[3]

[1] *Compt. Rend.* 1878, **87**, 578. [2] *Compt. Rend.* 1881, **93**, 63.

[3] See Cleve, *Journ. Chem. Soc.* 1895, i. 476, where a complete list of these is given.

GROUP IV.

Carbon.	Tin.
Silicon.	Cerium.
Titanium.	Lead.
Germanium.	Thorium.
Zirconium.	

339 In this group, as well as in Group V., there is no well-defined division of the elements composing it into two distinct sub-groups, such as is noticeable in the remaining five of the first seven groups; in certain details differences are observable between the members of the odd and even series, but these are of only minor importance, and the elements are therefore described throughout in the order of their atomic weight.

The first two members of this group, carbon and silicon, have already been described among the non-metallic elements. Both exist in the amorphous and crystallised states, silicon melting only at a very high temperature, whilst carbon has not yet been melted, although it volatilises at the highest attainable temperatures. The remaining elements have all metallic properties, and, with the exception of tin and lead, possess high melting points; in the compact state they undergo at most a surface oxidation in the air at the ordinary temperature, but when strongly heated readily combine with oxygen, and except in the case of lead, the oxide formed in presence of an excess of oxygen is the *dioxide*. The dioxides of the members having the lower atomic weights, including those of carbon and silicon, behave chiefly as acid-forming oxides, but they become more basic as the atomic weight of the element increases. These oxides correspond in each case with a series of salts in which the element is tetravalent, and except in the case of lead this series includes the most important compounds. Lead in its most characteristic compounds is divalent, and, as is so frequently the case with elements having a high atomic weight, it presents many resemblances to the elements having the next lowest and next highest atomic weights, viz., thallium and bismuth.

A very characteristic series of double salts with the alkali-haloids is yielded by the tetrahalogen derivatives of most of these elements, the double fluorides, which have the general formula $M^{I}_{2}M^{IV}F_{6}$, being the most important. In the case of

silicon, titanium, germanium, zirconium and tin, these compounds are isomorphous, but this appears not to be the case with the thorium compound. The corresponding salt of lead has not been prepared, but it yields an acid salt, $PbF_4,3KF,HF$, which is isomorphous with the analogous tin salt, $SnF_4,3KF,HF$.

Carbon is distinguished from all other elements by the property possessed by its atoms of uniting together in open or closed chains, forming nuclei, which may contain as many as sixty atoms, and which, in combination with the other elements, give rise to the immense number of carbon compounds. The same property is observable to a very small extent in silicon, but not in the other members of the group. In addition to the typical elements, carbon and silicon, only germanium, tin and lead, *i.e.*, the members of the "odd" series, yield organometallic derivatives.

Carbon and its simpler compounds, and the derivatives of silicon, have already been described in vol. i.

TITANIUM, Ti = 47·59.

340 The Rev. William Gregor[1] in 1789 discovered a new metal contained in the mineral menachanite or ilmenite, occuring in Cornwall. In 1795 Klaproth investigated the composition of the mineral rutile, and discovered in it a new metal to which he gave the name of titanium. In a subsequent investigation of ilmenite in 1797, he found that the metal which that mineral contained was titanium. Klaproth found that rutile consisted mainly of titanium dioxide, but he did not succeed in obtaining the oxide in the pure state, this having been first accomplished in 1821 by Rose.

Titanium is a rare metal, and is not found in the metallic state. It occurs as the dioxide TiO_2 in three minerals, rutile, brookite, and anatase, which possess different crystalline forms (see vol. i., p. 870), and also in combination with ferrous and ferric oxides in titanic iron ore or ilmenite $(FeTi)_2O_3$; and with lime and oxide of iron in perofskite $(CaFe)TiO_3$, as well as in titanite or sphene, $CaTiSiO_5$; schorlomite, $Ca(TiFe)SiO_5$, and keilhauite, $CaY(TiAlFe)SiO_5$. Magnetic iron ore also frequently contains larger or smaller quantities of titanium dioxide, and this titanium finds its way into many blast-furnace slags and pig-irons.

[1] *Crell. Ann.* 1791.

Titanium occurs in small quantity in several other minerals, and traces have been found in trap and basalt, in many amphiboles and micas, and in garnet, and hence it occurs in most fertile soils, in many clays, and likewise in certain mineral waters. It does not appear to occur in the animal or vegetable kingdom, but its presence has been detected in certain meteorites, and it forms an important constituent of the solar atmosphere.

Preparation of Metallic Titanium.—It appears very doubtful whether metallic titanium has yet been obtained in the pure condition; the usual methods for the reduction of the oxide, such as heating with metallic sodium and magnesium, yield products which still contain considerable quantities of titanium monoxide, and the product obtained by the action of sodium on halogen derivatives of titanium also usually contains small quantities of monoxide, formed by the action of the moisture present, and of the nitride, obtained by the direct union of the metal with nitrogen, which it is almost impossible to completely exclude. Owing to the extreme readiness with which titanium and nitrogen combine at high temperatures, and the metallic appearance of the nitride, this compound was mistaken by the earlier investigators for the metal itself, as was also the case with the compound which it forms with carbon and nitrogen, now known as titanium cyanonitride.

The nearest approach to the pure element has been obtained by Moissan, who fused carbon with an excess of titanium dioxide at a very high temperature in the electric furnace. Three distinct layers are found in the solidified product, the uppermost consisting of titanium containing about 5 per cent. of carbon, the second of the nitride, and the third of titanium monoxide. If the top layer be heated again with an excess of titanium dioxide, the quantity of carbon is reduced to 2 per cent., and the product is free from nitrogen and silicon.[1] Thus prepared titanium has a brilliant white fracture, and is hard enough to scratch rock crystal and steel, but is extremely friable. It has a specific gravity of 4·87, and on heating combines with the halogens and oxygen with incandescence. It dissolves in cold dilute sulphuric acid with evolution of hydrogen, and also in hot concentrated hydrochloric acid, aqua regia, and more slowly in nitric acid, and decomposes steam at 700—800°.

Nilson and Petersson[2] prepared metallic titanium by enclosing the requisite quantities of titanium tetrachloride and sodium in

[1] Moissan *Compt. Rend.* 1895, **120**, 290. [2] *Zeit. Phys. Chem.* 1887, **1**, 25.

an air-tight cylinder of mild steel, and exposing the latter to a red heat. The metal is thus obtained in yellow scales, which have frequently a bluish surface colour. These, however, still contain a considerable quantity of oxygen, probably as the monoxide. A still less pure product is obtained by heating potassium titanofluoride with sodium; the amorphous powder thus obtained resembles reduced iron in appearance, and contains oxygen and usually nitrogen in addition.

Titanium combines with nitrogen with extreme readiness, in this respect resembling boron and magnesium; the reaction commences at about 800°, and the nitride is also formed together with the oxide when the metal burns in the air.

TITANIUM COMPOUNDS.

Titanium and Oxygen.

341 Titanium combines with oxygen to form a number of oxides, the most important being:

Titanium dioxide, TiO_2.
Titanium sesquioxide, Ti_2O_3.
Titanium peroxide, TiO_3.

In addition to these the monoxide TiO has been prepared, and oxides of the formula Ti_3O_4, Ti_3O_5, Ti_7O_{12} have been described; the existence of the last three is, however, doubtful.

Titanium Dioxide, TiO_2, is trimorphous, occurring as three different minerals, rutile, anatase, and brookite; rutile crystallises in quadratic prisms (Fig. 150), having a specific gravity of 4·18—4·25, isomorphous with those of tin dioxide or cassiterite, and possessing an adamantine lustre, and a brown or reddish colour. Anatase crystallises in a totally different form of the quadratic system (Fig. 151), has a specific gravity of 3·82—3·95, and a brown or black colour. Brookite crystallises in flat rhombic prisms, and has a specific gravity of 3·86—4·23.

Amorphous titanium dioxide is obtained by the decomposition of aqueous chloride of titanium by ammonia, the precipitate being washed, dried, and ignited; or it may be directly prepared from rutile or titanic iron-ore. In order to prepare the pure oxide from rutile, the finely-powdered mineral is fused with

three times its weight of potassium carbonate, the solidified mass powdered and dissolved, in a platinum vessel, in dilute hydrofluoric acid, in which case potassium titanofluoride is formed, and the ferric oxide left free from titanium. The mass is then heated with sufficient water to dissolve the whole of the titanium double salt, the liquid boiled and filtered hot. On cooling, the mass of the titanofluoride crystallises out, and this, after washing with cold water, may be purified by re-crystallisation. The titanofluoride is then dissolved in hot water, and the titanium precipitated by ammonia, as titanic hydrate containing ammonia, which on ignition yields pure titanium dioxide (Wöhler). Pure titanic oxide may also be obtained from titanic iron-ore in a similar manner, or by fusing

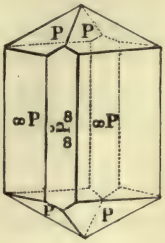


FIG. 150.

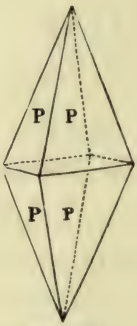


FIG. 151.

it with potassium bisulphate, or by igniting it in a mixture of chlorine and hydrochloric acid when ferric chloride is volatilised (Friedel and Guérin):

$$2FeTiO_3 + 4HCl + Cl_2 = 2FeCl_3 + 2TiO_2 + 2H_2O.$$

Amorphous titanium dioxide is a white tasteless powder, which when gently heated has a lemon-yellow colour, and when strongly ignited appears brown. It has a specific gravity of from 3·89 to 3·95, and when very strongly heated its specific gravity rises to 4·25.

When it is heated with microcosmic salt (Ebelmen) or with borax (G. Rose) for some time to a white-heat, fine crystals of rutile are obtained, which have a specific gravity of 4·26. Crystalline titanium dioxide can also be obtained by strong ignition of the fluoride in a current of moist air and hydrogen;

thus Hautefeuille[1] has shown that by treatment at a temperature not exceeding the boiling-point of cadmium (860°), anatase is produced, the crystals of which have a specific gravity of 3·7 to 3·9; at a temperature of about 1,000°, steel-blue coloured, rhombic crystals of brookite are obtained, which have a specific gravity of 4·1, and closely resemble the natural crystals from Miask. At still higher temperatures again, rutile is produced, so that this last is the only form which is stable at a high temperature, and in an acid or moist atmosphere.[2]

At the temperature of the oxy-hydrogen flame titanium dioxide fuses, forming a thin liquid, which solidifies to a confused crystalline mass.

In its chemical properties titanium dioxide closely resembles the corresponding silicon dioxide, behaving as an acid anhydride. It is insoluble in water, hydrochloric acid and dilute sulphuric acid, although it dissolves when digested for some time with hot concentrated sulphuric acid. The amorphous oxide dissolves on fusion with alkalis or alkali carbonates unless it has been strongly ignited, forming the titanates, and also dissolves slowly in fused potassium hydrogen sulphate, yielding a clear mass which dissolves perfectly in warm water. When this solution is boiled, the hydrated dioxide is precipitated. Titanium dioxide corresponds to the most important series of titanium salts in which the metal is tetravalent.

Titanium Monoxide, TiO, is obtained in the form of black prismatic crystals by heating the dioxide strongly in the electric furnace,[3] and is also formed together with magnesium titanate when titanium dioxide is heated with the requisite quantity of magnesium powder.[4]

$$2TiO_2 + 2Mg = TiO + MgTiO_3.$$

Titanium Sesquioxide, Ti_2O_3, is obtained by strongly igniting titanium dioxide in a current of hydrogen, and allowing the product to cool in the gas. The same oxide may also be obtained as a copper-coloured lustrous crystalline mass, together with the sesquichloride and oxychloride of titanium by passing a mixture of hydrogen and the vapour of titanium chloride over white-hot titanium dioxide. It is not attacked by nitric or

[1] *Ann. Chim. Phys.* 1865 [4], **4**, 129.
[2] Friedel and Guérin, *Bull. Soc. Chim.* 1874, **22**, 482.
[3] Moissan, *Compt. Rend.* 1892, **115**, 1034.
[4] Winkler, *Ber.* 1890, **23**, 2658.

hydrochloric acid, and sulphuric acid dissolves it with formation of a violet solution (Ebelmen).

The *hydrated sesquioxide* is formed by digesting a solution of titanic acid in hydrochloric acid with metallic copper at from 20° to 40°; the solution attains a violet-blue colour, and when poured into aqueous ammonia, yields a dark-brown precipitate of titanous hydroxide (Fuchs). The hydroxide is also formed when a solution of the trichloride is precipitated by alkalis.

Ilmenite, or *Titanic Iron-ore*, $(FeTi)_2O_3$.—This mineral, the one in which titanium was first discovered, occurs tolerably widely distributed, and crystallises in black hexagonal crystals, isomorphous with hæmatite. One of its most important localities is Krageroe, in Norway. Fine crystals are also found at Warwick Co., New York, and vast deposits occur at Bay St. Paul, in Canada. It is frequently found in the finely-divided state as sand on the shores of the Mersey opposite Liverpool, in New Zealand, and elsewhere. Its specific gravity ranges from 4·5 to 5, and its composition is a variable one. It is usually considered to be a mixture of ferrous titanate with ferric oxide, but its isomorphism with the latter, and the fact that when it dissolves in acids it yields the same colour as titanium sesquioxide renders Rose's view probable that it is an isomorphous mixture of the sesquioxides of iron and titanium.

Titanium Trioxide, or *Titanium Peroxide*, TiO_3 is obtained by dropping titanium chloride into dilute alcohol, and adding a large excess of hydrogen dioxide to the solution. Ammonia, ammonium carbonate, or potash is then added, and after a time a bright yellow precipitate separates out. The precipitate consists of a hydrate of titanium trioxide, which retains water and salts very persistently, and dissolves in hydrochloric acid with evolution of a little chlorine and formation of a yellowish-red solution.[1]

Titanic Acid and the Titanates.

342 As is the case with the analogous silicic acid, a number of hydrates of varying composition is known. There appears to be little doubt that the hydrates orthotitanic acid, $Ti(OH)_4$, and metatitanic acid, $TiO(OH)_2$, exist, but in addition others have been prepared containing quantities of water intermediate between the amounts required for these two formulæ, and also with

[1] Classen, *Ber.* 1888, **21**, 370

less than that required by the latter formula. These may possibly be the hydrates corresponding to the complex titanic acids, but they have not been obtained of sufficiently definite composition to enable this to be ascertained.

Orthotitanic Acid, $Ti(OH)_4$, is obtained by adding an alkali to a cold hydrochloric acid solution of a titanate, and forms a voluminous white precipitate, which is soluble in dilute hydrochloric acid and sulphuric acid, and loses water on drying, forming other hydrates. When heated it is converted into the anhydride, the reaction being accompanied by evolution of light. When allowed to remain under water it is gradually converted into metatitanic acid.[1]

Metatitanic Acid, $TiO(OH)_2$, is obtained by boiling solutions of orthotitanic acid in hydrochloric acid, or by the action of nitric acid of specific gravity 1·25 on titanium. It is insoluble in acids with the exception of concentrated sulphuric acid. When heated it is converted into the anhydride without evolution of light.

The other hydrates are frequently also spoken of as "ortho" or "meta" acids, according as they are soluble or insoluble in dilute acids.

By the dialysis of a hydrochloric acid solution of orthotitanic acid, Graham obtained a solution of titanic acid, and v. der Pfordten has also obtained the acid as a colourless jelly.[2]

Potassium Titanate, K_2TiO_3, is formed as a yellow fibrous mass when the dioxide is fused with potassium carbonate. On boiling titanic acid with caustic potash, and evaporating the solution, colourless, readily soluble prisms of $K_2TiO_3+4H_2O$ are deposited. When a hydrochloric acid solution of titanic acid is precipitated with potassium carbonate, an amorphous precipitate of potassium trititanate, $K_2Ti_3O_7+2H_2O$, is thrown down, and this in presence of hydrochloric acid is converted into a hexatitanate, $K_2Ti_6O_{13}+2H_2O$. The fused anhydrous normal salt, when treated with water in excess, also yields a trititanate, $K_2Ti_3O_7+3H_2O$, as a fine crystalline powder.

Calcium Titanate, $CaTiO_3$.—This occurs in the Urals, in the valley of Zermatt in Switzerland, and at Magnet Cove, Arkansas, as the mineral perofskite, which contains in addition 1 to 6 per cent. of ferrous oxide, as well as traces of manganese and magnesium. It forms rhombic crystals having a metallic or adamantine lustre, a yellow or iron-black colour, and a specific

[1] Wagner, *Ber.* 1888, **21**, 960. [2] *Annalen*, 1887, **237**, 213.

gravity of 4·0. The crystals can be artificially obtained by strongly igniting a mixture of titanium dioxide, lime, and calcium carbonate (Ebelmen).

Calcium Titanosilicate, $CaTiSiO_5$, is found as titanite or sphene in brown, green, or black monosymmetric crystals, having an adamantine or resinous lustre and a specific gravity of 3·4 to 3·56, occurring imbedded in granite gneiss, mica-schist, and granular limestone. Titanite can be obtained artificially by fusing calcium chloride with titanium dioxide and silica. The mineral guarinite has the same composition as titanite, and is found in quadratic crystals, having a specific gravity of 3·487, in small cavities in a greyish trachyte at Monte Somma.

Titanium and the Halogens.

343 *Titanium Trifluoride*, TiF_3, is obtained as a violet powder by igniting potassium titanofluoride in a current of hydrogen, and treating the product with hot water. It combines with ammonium fluoride, forming several double salts.

Titanium Tetrafluoride, TiF_4, is obtained as a fuming, colourless liquid when a mixture of titanium dioxide and fluorspar is distilled with fuming sulphuric acid in a platinum vessel (Unverdorben). When titanium dioxide is dissolved in hydrofluoric acid, a syrupy liquid is obtained, which probably contains *hydrogen titanofluoride*, H_2TiF_6. The *titanofluorides* are isomorphous with the silicofluorides, zirconofluorides, and stannofluorides.

Potassium Titanofluoride, $K_2TiF_6 + H_2O$.—This salt is prepared either by adding potash to aqueous hydrogen titanofluoride (Berzelius), or, according to Wöhler, by fusing titanium dioxide in a platinum crucible with twice its weight of potassium carbonate and dissolving the fused and pulverised mass, in a platinum dish, in the requisite quantity of dilute hydrofluoric acid. The potassium salt then crystallises out in shining scales closely resembling those of boric acid and belonging to the monosymmetric system (Marignac), which may be dried between filter paper, and recrystallised from boiling water. It loses its water at 100°, and melts without decomposition at a white-heat.

Sodium Titanofluoride, Na_2TiF_6, is obtained in a similar manner to the preceding salt in hexagonal prisms most probably isomorphous with sodium silicofluoride (Marignac). A solution containing an excess of hydrofluoric acid deposits small glistening rhombic crystals having the composition $Na_2TiF_6 + NaHF_2$.

Ammonium Titanofluoride, $(NH_4)_2TiF_6$.—This salt was obtained by Berzelius in rhombohedra isomorphous with the corresponding tin compound, by neutralising hydrogen titanofluoride with ammonia. A second ammonium salt having the composition $(NH_4)_2TiF_6 + NH_4F$ separates in quadratic crystals from a solution of the preceding salt in an excess of fluoride of ammonium.

344 *Titanium Dichloride*, $TiCl_2$, was obtained by Friedel and Guérin[1] by passing dry hydrogen at a dark red-heat over titanium trichloride. This compound is a very hygroscopic light-brown powder, which can be volatilised in hydrogen at a red-heat without fusion. It burns like a tinder on exposure to air, giving off fumes of titanium tetrachloride and leaving a residue of titanium dioxide. It hisses when thrown into water, evolving hydrogen and yielding a yellow liquid.

Titanium Trichloride, $TiCl_3$.—When the vapour of titanium tetrachloride mixed with hydrogen is passed through a red-hot tube, dark violet scales of the trichloride are deposited (Ebelmen). It may also be obtained by heating titanium tetrachloride in a closed tube with molecular silver to a temperature of from 180 to 200°:

$$TiCl_4 + Ag = TiCl_3 + AgCl.$$

If the mixture thus obtained be heated more strongly, the reverse action takes place (Friedel and Guérin). Titanium trichloride is non-volatile and on heating decomposes into the dichloride and tetrachloride. When heated in the air, thick vapours of titanium tetrachloride are emitted and titanium dioxide is left behind. It readily deliquesces on exposure to moist air, and dissolves in water with evolution of heat, yielding a reddish-violet solution.

Titanium trichloride is a powerful reducing agent. Thus when boiled with aqueous sulphurous acid, sulphur separates out, and the salts of gold, silver, and mercury are reduced by it to metal.

Titanium Tetrachloride, $TiCl_4$.—Metallic titanium does not combine with chlorine at the ordinary temperature, but when heated it burns in the gas with brilliancy, forming the tetrachloride (Wöhler). According to Friedel and Guérin, titanium dioxide is converted, in presence of chlorine at a white-heat, into titanium tetrachloride with evolution of oxygen. The

[1] *Ann. Chim. Phys.* 1876 [5], **7**, 24.

tetrachloride is, however, best obtained by passing dry chlorine over a heated mixture of titanium dioxide and carbon. Titanium tetrachloride is a mobile, transparent, colourless liquid, having a specific gravity of 1·7604 at 0° (Pierre). It freezes at −25°, and boils at 136·4°, its vapour having a specific gravity of 6·836 (Dumas). It possesses a penetrating acid smell, and emits dense white fumes on exposure to air.

Titanium tetrachloride is decomposed by an excess of water with formation of titanic acid, which remains dissolved in the aqueous hydrochloric acid simultaneously formed. By careful addition of water it is possible to replace the chlorine atoms one by one by hydroxyl yielding the compounds $TiCl_3OH$, $TiCl_2(OH)_2$, and $TiCl(OH)_3$.

Titanium tetrachloride yields a large number of crystalline compounds with other chlorides analogous to those formed by stannic chloride. When dry ammonia gas is passed over titanium tetrachloride, it is rapidly absorbed, and a very hygroscopic powder, $TiCl_4+4NH_3$, is formed, which when ignited yields a yellow sublimate of $TiCl_4+3NH_4Cl$.

Titanium Oxychloride, $Ti_2O_2Cl_2$, is obtained, together with the dichloride, when a mixture of hydrogen and the vapour of titanium tetrachloride is passed over the ignited dioxide. It forms reddish-brown translucent crystals, which burn when heated in the air with formation of the dioxide and tetrachloride (Friedel and Guérin). Other oxychlorides have also been prepared.

Titanium Tetrabromide, $TiBr_4$, is obtained when hydrobromic acid is passed over the chloride,[1] as an amber-yellow hygroscopic, finely crystalline mass which has a specific gravity of 2·6, melts at 39°, and boils at 230°.[2]

Titanium Tetriodide, TiI_4, is produced when iodine vapour is passed over ignited titanium (Weber); also when dry hydriodic acid is passed into titanium tetrachloride, which is gradually heated up to its boiling-point. The small quantity of free iodine giving a violet tinge may be removed by three or four distillations in a stream of hydrogen (Hautefeuille). A third process consists in passing the vapour of titanium tetrachloride mixed with hydrogen and iodine vapour through a tube heated to redness. Titanium tetriodide forms a brittle mass having a reddish-brown colour and metallic lustre. It melts at 150° to a

[1] Thorpe, *Journ. Chem. Soc.* 1885, i. 126.
[2] Duppa, *Proc. Roy. Soc.* 1857, **8**, 42.

yellowish-brown liquid, which solidifies on cooling in fine octohedral crystals. It distils without decomposition at a temperature slightly above 360°, giving rise to orange-coloured vapours. The specific gravity of its vapour at 440° has the normal value of 18·054. It fumes strongly in the air and dissolves readily in water.

Titanium and Sulphur.

345 Titanium combines with sulphur to form the sulphides, TiS_2, Ti_2S_3, and TiS, corresponding to the oxides of the metal.

Titanium disulphide, TiS_2, is obtained by passing a mixture of titanium tetrachloride vapour and sulphuretted hydrogen through an ignited tube, and forms large brass yellow lustrous scales, closely resembling mosaic gold. It burns when ignited in the air, yielding titanium dioxide and sulphur dioxide.

Titanium sesquisulphide, Ti_2S_3, is formed by passing a mixture of moist sulphuretted hydrogen and carbon bisulphide vapour over titanium dioxide heated to bright redness,[1] or by igniting the disulphide in a current of an indifferent gas,[2] and forms a greenish-black or grey powder.

Titanium monosulphide, TiS, is prepared by heating either of the foregoing compounds in a current of hydrogen, and is a lustrous substance resembling bismuth.

Titanium Sesquisulphate, $Ti_2(SO_4)_3 + 8H_2O$, is obtained by dissolving the metal in dilute sulphuric acid. The violet solution on concentration assumes a fine blue lustre, and deposits small tufts of crystal (Glatzel). It forms an alum with cæsium sulphate, $Cs_2SO_4,Ti_2(SO_4)_3+24H_2O$, which crystallises in cubes.[3]

Normal Titanium Disulphate, $Ti(SO_4)_2+3H_2O$, is formed by the oxidation of the sesquisulphate with nitric acid, and on evaporation remains as a transparent yellowish deliquescent amorphous mass. If the calculated quantity of potassium sulphate be added to this solution and the mixture allowed to evaporate over sulphuric acid, crystals of the double salt $K_2SO_4+Ti(SO_4)_2+3H_2O$ separate out.

Basic Titanium Sulphate, $(TiO)SO_4$, is obtained as a white hard mass by dissolving dry titanic acid in boiling sulphuric acid and evaporating.[4]

[1] Thorpe, *Journ. Chem. Soc.* 1885, i. 491.
[2] v. d. Pfordten, *Annalen*, 1886, **234**, 290.
[3] Piccini, *Gazzetta*, 1895, **25**, ii. 542.
[4] Merz, *J. Pr. Chem.* 1866, **99**, 157.

Titanium and Nitrogen.

346 Titanium is distinguished from most of the elements by the extreme readiness with which it combines with nitrogen. Several compounds of these two elements are known.

Normal titanium nitride, Ti_3N_4, is obtained as a copper-coloured substance by heating ammonio-chloride of titanium, $TiCl_4,4NH_3$, by itself (H. Rose), or better in a stream of ammonia gas.[1] This was originally supposed to be metallic titanium, but Wöhler[2] proved that it consisted of a nitride of titanium having the above composition.

Titanium Dinitride, TiN_2, is obtained as a dark-blue powder, having a copper-red lustre resembling sublimed indigo, by strongly igniting titanium dioxide in a current of ammonia gas (Wöhler).

Titanium Mononitride, TiN or Ti_2N_2, is obtained by heating titanium dioxide very strongly in the electric furnace in presence of nitrogen, and is a bronze-yellow mass which has a specific gravity of 5·18, and is hard enough to scratch rubies and cut diamonds.[3]

Titanium and Carbon.

347 *Titanium Carbide*, TiC, is obtained by fusing titanium dioxide with an excess of carbon in the electric furnace, and is thus obtained as a mass having a crystalline fracture, and a specific gravity of 4·25; it is not attacked by hydrochloric acid, is only slowly dissolved by aqua regia, and does not decompose steam at 700°. In other respects it closely resembles metallic titanium, but burns more readily in oxygen.[4]

Steel-grey crystals of titanium carbide have also been obtained from cast iron prepared from ores containing titanium.[5]

Titanium Cyano-nitride.—When iron ores containing titanium are reduced in the blast-furnace, small brilliant copper-coloured cubes, which are hard enough to scratch glass, and are almost

[1] Liebig, *Pogg. Ann.* 1830, **21**, 259.
[2] *Annalen*, 1850, **73**, 34.
[3] Moissan, *Compt. Rend.* 1895, **120**, 290.
[4] Moissan, *loc. cit.*
[5] Shimer, *Chem. News*, 1887, **55**, 156.

infusible, are found in cavities both of the slag and of the metal. A mass containing as much as 80 lbs. has been found in a single blast-furnace in the Harz. This substance was examined by Wollaston in 1822 and believed by him to be metallic titanium;[1] but Wöhler in 1849 showed that it contained nitrogen and cyanogen, and gave to it the formula $Ti(CN)_2+3Ti_3N_2$. He likewise obtained it artificially[2] by heating a mixture of ferrocyanide of potassium and titanium dioxide in a well-closed crucible at a temperature sufficient to melt nickel. Titanium cyano-nitride can also be prepared by heating to whiteness a mixture of titanium dioxide and charcoal in a tube of gas-carbon in a stream of dry nitrogen (Deville and Wöhler).[3] A third method of preparation is to fuse potassium cyanide in the vapour of titanium tetrachloride (Wöhler). It has a specific gravity of 5·28, and is only attacked by a mixture of nitric and hydrofluoric acids. When ignited in a current of steam it is decomposed as follows:

$$Ti(CN)_2+3Ti_3N_2+20H_2O=2HCN+10TiO_2+6NH_3+10H_2.$$

Chlorine also decomposes this substance at a red-heat, titanium tetrachloride and a volatile sublimate consisting of a compound of titanium tetrachloride and cyanogen chloride being formed. When fused with potash ammonia is given off, potassium titanate being produced.

Detection and Estimation of Titanium.

348 Titanium is distinguished from tin inasmuch as its oxides are not reduced to the metallic state when heated on charcoal before the blowpipe. With microcosmic salt titanium dioxide yields a colourless bead in the outer flame but in the inner flame the bead is yellow whilst hot and assumes a violet colour on cooling According to Riley the delicacy of this reaction is increased by melting metallic zinc in the microcosmic bead heated on charcoal, a distinct coloration being then obtained, when the zinc is burnt away, even with minute quantities of titanium. When fused in the microcosmic bead with addition of a small quantity of an iron salt in the reducing flame a

[1] *Phil. Trans.* 1823, 17. [2] *Annalen*, 1850, **73**, 34; **74**, 212.
[3] *Annalen*, 1857, **103**, 230.

bright-red bead is obtained. Titanium compounds do not colour the gas-flame, but the spark-spectrum and that in the electric arc show an enormous number of bright lines, chiefly in the blue and green, which have been carefully mapped by Thalén and others.

Metallic zinc placed in a hydrochloric acid solution of titanic acid evolves hydrogen and the liquid assumes a violet-blue colour, a dark violet precipitate being formed if the solution be not too dilute, and this gradually turns white by oxidation. The violet-blue solution when diluted with water assumes a rose-colour, and this reaction serves for the detection of small quantities of titanium. Sodium thiosulphate when boiled with a nearly neutral solution of a titanate precipitates the whole of the titanic acid, and this reaction serves as a means of separating titanium from iron and the metals of the cerium group.

In order to remove silica, when present, the mixture is evaporated with hydrofluoric acid, the silicon being expelled as silicon tetrafluoride.

Titanium is always determined *quantitatively* in the form of titanium dioxide, this being thrown down from its solutions in acids by ammonia. Titanium may also be determined volumetrically by reducing titanium dioxide to titanium sesquioxide by means of zinc in an acid solution and subsequently oxidising with standard permanganate.

Atomic Weight of Titanium.—The atomic weight of titanium was first determined by Rose[1] in 1829 by decomposing titanium tetrachloride with water, weighing the titanic acid formed, and estimating the chlorine in the filtrate, the number found being 47·72 (O = 15·88). A redetermination was made in 1885 by Thorpe,[2] who analysed pure titanium tetrachloride and tetrabromide, the amount of silver required for complete precipitation of the halogen, the amount of silver haloid formed, and the quantity of titanium dioxide yielded by each being ascertained; the average of the results of the six series of experiments gave the number 47·59.

[1] *Pogg. Ann.* 1829, **15**, 145.
[2] *Journ. Chem. Soc.* 1885, i. 108.

GERMANIUM Ge = 71·8.

349 This element was discovered in 1886 by Winkler in the course of an investigation of a new silver mineral found at Freiberg in 1885, and termed argyrodite, $GeS_2,3Ag_2S$. The preliminary investigation led him to suppose that the new element would occupy the vacant place between antimony and bismuth in the periodic classification,[1] but further examination showed that the new element was tetravalent and identical with the ekasilicon predicted by Mendeléeff. The close agreement between the predicted properties of the element and its compounds, and those actually observed by Winkler has already been mentioned (p. 62).

Germanium is an extremely rare element, having only been found in the above mineral and also to the extent of 0·1 per cent in euxenite.[2] Its compounds are for the most part tetravalent, and closely resemble those of silicon and the other tetravalent elements.

Metallic germanium is best obtained by the reduction of germanium dioxide with carbon at a full red-heat. The semi-crystalline regulus is washed with water to remove carbon and fused with a little borax. It is thus obtained as a greyish-white brittle lustrous metal, which frequently crystallises in octohedra, has a specific gravity of 5·469, melts at 900°, and is not markedly volatile at 1350°. It oxidises at a high temperature, is insoluble in hydrochloric acid, but dissolves in aqua regia, and is converted by nitric acid into the dioxide. It combines directly with the halogens.

COMPOUNDS OF GERMANIUM.

350 Germanium forms two oxides, germanium dioxide, GeO_2, and germanium monoxide, GeO.

Germanium Dioxide, GeO_2, is the most important of these and is obtained from argyrodite as follows: the powdered mineral is mixed with nitre and potassium carbonate, and the mixture introduced in small quantities at a time into a red-hot

[1] *Ber.* 1886, **19**, 210. [2] Krüss, *Ber.* 1888, **21**, 131.

Hessian crucible. On cooling two layers are obtained, and the upper one, which contains all the germanium, is powdered, extracted with water, the solution treated with sulphuric acid and evaporated to dryness. The acid residue dissolves in cold water, but almost all the germanium is deposited as oxide on standing; the remainder is precipitated as sulphide and converted into oxide by heating with nitric acid. To purify the crude oxide it is dissolved in hydrofluoric acid, and potassium fluoride added; potassium germaniofluoride separates out, and is converted into a soluble thio-salt by fusion with potassium carbonate and sulphur, this being decomposed by sulphuric acid, and the germanium precipitated as sulphide with sulphuretted hydrogen. The sulphide when mixed with a little sulphuric acid and heated yields a mixture of sulphide and oxide, which is converted into the pure oxide by roasting and treating with nitric acid. Thus prepared it forms a dense white powder, which is somewhat soluble in water, 1 part of the dioxide dissolving in 247·1 parts of water at 20°, and in 95·3 parts at 100°; the solution on evaporation deposits microscopic rhombic crystals. Germanium dioxide has acid properties but also dissolves in acids; it is readily reduced by carbon, sodium and magnesium.

No germanium hydroxide of definite composition has been obtained, but a colloidal hydrate is obtained by precipitating an alkaline solution of the dioxide with carbon dioxide.

Germanous Oxide, GeO, is obtained by heating the dioxide with a small quantity of magnesium or by heating the hydroxide and forms a greyish-black powder. The corresponding *hydroxide*, $Ge(OH)_2$, is obtained as a yellow or yellowish-red precipitate by the action of alkalis on germanium dichloride or germanium chloroform.

Germanium Salts.

351 *Germanium Tetrafluoride*, GeF_4 has not been obtained in the anhydrous state, but large crystals containing three molecules of water are obtained by concentrating a solution of the dioxide in hydrochloric acid. It combines with hydrofluoric acid to form *germanofluoric acid*, which has not been prepared pure; its *potassium* salt, K_2GeF_6, is prepared by adding potassium fluoride to a solution of the dioxide in hydrofluoric acid, and forms hexagonal crystals isomorphous with those of ammonium silicofluoride, which are sparingly soluble in cold, but readily in hot water.

Germanium Tetrachloride, $GeCl_4$, is obtained by the direct union of germanium and chlorine, but is best prepared by heating the metal or the sulphide with mercuric chloride; it is a thin colourless liquid, which fumes in the air, has a specific gravity of 1·887 at 18°, and boils at 86°. It is slowly decomposed by water with formation of hydrated germanium dioxide.

Germanium Chloroform, $GeHCl_3$.—When germanium is heated in a current of hydrogen chloride, it becomes red-hot and a distillate is obtained, which, after exposure to the air, separates into two layers. The heavier of these consists of germanium chloroform, which is a colourless fuming liquid, boiling at 75°. The lighter layer is *germanium oxychloride*, $GeOCl_2$, which is also a colourless liquid, but is less mobile than germanium chloroform, and does not fume in the air; it boils considerably above 100°. *Germanium dichloride*, $GeCl_2$, is also known.

Germanium Disulphide, GeS_2.—This compound, which is the most characteristic of the germanium derivatives, is prepared by the action of sulphuretted hydrogen on a solution of germanium dioxide, or by the addition of an excess of mineral acids to a solution of an alkaline thiogermanate, sulphuretted hydrogen being passed through the solution to complete the precipitation. It is a white powder, which is only wetted with difficulty by water, in which however it is appreciably soluble, 1 part dissolving in 221·9 parts of cold water, and it also readily dissolves in ammonium sulphide. The thiogermanate is obtained by fusing germanium derivatives with an alkali carbonate and sulphur.[1]

Germanium Monosulphide, GeS, is obtained by carefully heating the disulphide in a current of hydrogen, and forms thin plates having a greyish-black colour and an almost metallic lustre. The reduction easily proceeds further, with formation of metallic germanium. When dissolved in alkalis and reprecipitated by acid, it forms brown amorphous flakes which dissolve in hot concentrated hydrochloric acid with evolution of sulphuretted hydrogen.[2]

Detection and Estimation of Germanium.

352 Germanium salts impart no colour to the Bunsen flame, but the spark spectrum exhibits a number of bright lines, especially

[1] *J. Pr. Chem.* 1886 (2), **34**, 182; 1887 (2), **36**, 177.
[2] *Ber.* 1888, **21**, 131.

in the blue and violet regions, the following among others having been measured: 6021, 5893, 5131, 4814, 4743, 4685, 4261, 4179. It is most readily recognised by the formation of the white sulphide, soluble in excess of ammonium sulphide, and this compound is also the most suitable yet known for its gravimetric estimation. The atomic weight of germanium was determined by Winkler by the analysis of pure germanium chloride, the average value found being 71·8 (O = 15·88).

ZIRCONIUM Zr = 90·0.

353 In 1789 Klaproth found a new earth in the mineral zircon, to which he gave the name of zirconia. He discovered in 1795 that the same earth was contained in hyacinth, a mineral found in Ceylon, and he thus ascertained the truth of Werner's previous supposition that these two minerals were identical. Zircon and hyacinth possess the formula $ZrSiO_4$, and are more or less coloured by ferric oxide. Zirconium is likewise found in a few other rare minerals, and occurs in appreciable quantities in Norwegian granite, together with thorium and several of the rare earths.[1]

The metal zirconium was first obtained by Berzelius in the form of an iron-grey powder by heating potassium zirconofluoride with potassium. The metal also can be obtained, according to Troost, by passing the vapour of zirconium chloride, $ZrCl_4$, over ignited sodium. The ignited amorphous metallic powder thus obtained is so finely divided that it passes through the pores of filter-paper, but it assumes a metallic lustre under the burnisher. The amorphous metal may also be prepared by heating zirconia with magnesium powder.[2]

Crystallised zirconium was first prepared by heating potassium zirconofluoride with aluminium at the temperature of melting iron; it is however best prepared by heating zirconia in the electric furnace with an insufficient quantity of carbon for its complete reduction, and is thus obtained as a metallic button containing some zirconia but free from carbon and nitrogen. It may also be obtained by heating the carbide with zirconia in a similar manner.[3]

[1] Phipson, *Chem. News*, 1896, **73**, 145.

[2] Phipson, *Compt. Rend.* 1865, **61**, 745; Winkler, *Ber.* 1890, **23**, 2664.

[3] Moissan, *Compt. Rend.* 1893, **116**, 1222; Troost, *Compt. Rend.* 1893, **116**, 1428.

Crystallised zirconium forms broad apparently monosymmetric plates, has a specific gravity of 4·25, and is hard enough to scratch glass and rubies. It is only very slowly oxidised in the air even at a white-heat, but burns in the oxy-hydrogen flame, and yields the chloride when heated to a dull red-heat in chlorine or hydrochloric acid gas. It is also dissolved by caustic potash with evolution of hydrogen. It is only slowly attacked by acids with the exception of hydrofluoric, even on heating, but is rapidly oxidised by aqua regia. The amorphous metal readily takes fire on warming in the air.

ZIRCONIUM COMPOUNDS.

Zirconium and Oxygen.

354 *Zirconium Oxide or Zirconia*, ZrO_2.—In order to prepare this oxide zircon is ignited and then quenched in water. The powdered mineral is mixed with three to four times its weight of acid potassium fluoride and gently heated in a platinum vessel until all moisture has been driven off. The platinum crucible is then placed in a Hessian one and both well covered and exposed for two hours to the strongest heat of a wind-furnace. The porcelain-like mass thus obtained is boiled with water containing hydrofluoric acid and the insoluble potassium silicofluoride filtered off. On cooling the solution, crystals of potassium zirconofluoride are deposited and these purified by recrystallisation. The pure salt is then heated with sulphuric acid until all the hydrofluoric acid is driven off, the residue dissolved in water, and the zirconia precipitated in the cold by ammonia.[1]

In order to avoid the use of hydrofluoric acid, the very finely powdered zircon may be treated as follows. It is first fused with hydrogen potassium sulphate and the fused mass repeatedly boiled out with water containing sulphuric acid when a residue of basic zirconium sulphate, Zr_3SO_9, is obtained, which is next fused with caustic soda in a silver basin. This is then lixiviated with water, the residual zirconia, which contains soda, washed with hot water and dissolved in hot concentrated sulphuric acid, the solution filtered and precipitated with ammonia.[2] The

[1] Homberger, *Annalen*, 1876, **181**, 232.
[2] Franz, *Ber.* 1870, **3**, 58.

precipitate thus obtained consists of *zirconium hydroxide* $Zr(OH)_4$, which readily parts with its water on heating. The hydroxide is slightly soluble in water and colours yellow turmeric paper brown. When precipitated and washed in the cold it is easily soluble in dilute acids; if, however, it be precipitated from a hot solution, or washed with boiling water, it is only soluble in concentrated acids. When heated to incipient redness it is converted into zirconia with evolution of heat. The oxide thus obtained is only slightly soluble even in hydrofluoric acid but dissolves on heating in a mixture of two parts of sulphuric acid and one part of water. Zirconia can be obtained in the crystalline state in the form of quadratic prisms isomorphous with cassiterite and rutile and having a specific gravity of 5·71.[1] For this purpose the amorphous oxide is fused with borax in a porcelain furnace, the fused residue being boiled out with sulphuric acid.

Zirconia, like the dioxides of the other metals of this group acts as an acid-forming oxide, and yields salts corresponding to the metasilicates and metatitanates.

Sodium Zirconate, Na_2ZrO_3, obtained by fusing the oxide with sodium carbonate, forms a crystalline mass which is decomposed by water with separation of zirconia. When heated with an excess of sodium carbonate to whiteness the salt Na_4ZrO_4 is produced. This is again decomposed by water with formation of hexagonal tables having the composition $Na_2Zr_8O_{17}+12H_2O = Na_2O.8ZrO_2+12H_2O$.

The zirconates of calcium and magnesium are crystalline and insoluble in water.

Zirconium Peroxide, $Zr_2O_5+9H_2O$, is obtained as a white powder when hydrogen peroxide is added to a solution of zirconium sulphate. Under certain conditions a hydrated oxide ZrO_3+5H_2O is formed.[2]

Zirconium and Hydrogen.

355 When zirconia is heated with magnesium powder in a current of hydrogen, the latter is absorbed, the product containing probably zirconium hydride, ZrH_2, together with zirconia and perhaps a lower oxide.[3]

[1] Nordenskiold, *Pogg. Ann.* 1861, **114**, 612.
[2] Bailey, *Journ. Chem. Soc.* 1886, i. 481.
[3] Winkler, *Ber.* 1891, **24**, 888.

Zirconium Salts.

356 *Zirconium Fluoride*, ZrF_4, is obtained by heating zirconia with acid ammonium fluoride. The residual mass is easily soluble in water containing hydrofluoric acid and crystallises in glistening asymmetric tables having the composition $ZrF_4 + 3H_2O$.

Zirconium fluoride forms a series of double salts with other fluorides which are isomorphous with the corresponding silicofluorides, titanofluorides, and stannofluorides.

Potassium Zirconofluoride, K_2ZrF_6, is obtained by igniting zircon with acid potassium fluoride or by pouring a solution of potassium fluoride into an excess of zirconium fluoride solution. It crystallises from hot water in small acute rhombic prisms and dissolves at 2° in 128, at 15° in 71, and at 100° in 4 parts of water.

When zirconium hydroxide is dissolved in the smallest quantity of hydrofluoric acid, and the liquid poured into a concentrated solution of neutral potassium fluoride, the salt $K_2ZrF_6 + KF$ is precipitated, and crystallises from boiling water in fine needles.

If sodium fluoride and zirconium fluoride be mixed in any proportion, the salt $Na_2ZrF_6 + 4NaF$ is produced. It forms small monosymmetric crystals which dissolve in 258 parts of water at 18° and at 100° in about 60 parts of water.

Ammonium salts, corresponding to the salts of potassium, and other double fluorides, are known, which crystallise well and are usually soluble.

Zirconium Chloride, $ZrCl_4$, is obtained by passing chlorine gas over a heated mixture of zirconia and charcoal, or by the action of chlorine or hydrochloric acid gas on the heated metal. It may be recrystallised from hydrochloric acid, but it is doubtful whether it has ever been obtained free from the oxychloride. On addition of water, heat is evolved and zirconium oxychloride $ZrOCl_2$ formed, which remains dissolved in the acid solution. The same compound is obtained by dissolving zirconium hydroxide in dilute hydrochloric acid, and on evaporation crystallises out in prismatic needles belonging to the quadratic system, and having the composition $ZrOCl_2 + 8H_2O$.[1] These are readily soluble in water, have an astringent taste, and when heated to 50° lose water, forming more basic oxychlorides.

[1] Weibull, *Ber.* 1887, **20**, 1394.

Zirconium Bromide, $ZrBr_4$, is prepared in a similar way to the chloride and forms a white crystalline powder which is easily volatilised at the temperature of the gas-flame. In contact with moist air or water it forms zirconium oxybromide, $ZrOBr_2$, which crystallises in needles.

Zirconium Sulphide.—When metallic zirconium and sulphur are heated together in a current of hydrogen, they combine with evolution of heat to form a cinnamon-brown powder, which assumes a metallic lustre under the burnisher. This is not attacked by most of the dilute acids, but dissolves slowly in aqua regia and readily in hydrofluoric acid. When fused with potash, zirconia and potassium sulphide are formed.

Zirconium Sulphate, $Zr(SO_4)_2$, is obtained by dissolving the oxide or hydroxide in sulphuric acid, evaporating, and heating nearly to redness. It is a white mass which dissolves slowly but completely in cold, and quickly in hot water Hydrated crystals are obtained by concentrating a solution which contains free acid, and these swell up on heating like alum. The salt decomposes at a red-heat, leaving a residue of pure zirconia. If its solution be saturated with zirconium hydroxide a basic salt, $Zr(SO_4)_2 + ZrO_2$ or $(ZrO)SO_4$, is formed, and this is obtained on evaporation as a hydrated mass. If the normal salt be precipitated with alcohol an insoluble salt, $Zr(SO_4)_2 + 2ZrO_2$, is thrown down.

Zirconium Nitrate, $Zr(NO_3)_4$, is obtained as a yellow gummy mass by dissolving the hydroxide in nitric acid and evaporating at a moderate heat.

Zirconium Carbides.—Zirconium combines with carbon to form two different carbides having the composition ZrC_2 and ZrC. The former is obtained by heating zirconia with an excess of carbon in the electric furnace and has a metallic appearance and brilliant fracture, and is not decomposed by water even on heating. The *monocarbide* is prepared in a similar manner, but the mixture of zirconia and carbon is placed in a carbon tube closed at one end, which is then heated in the electric furnace. It has a grey colour and metallic lustre and is hard enough to scratch quartz. It is permanent in the air and is not decomposed by water, but burns brilliantly when heated strongly in oxygen.[1]

Silicates of Zirconium.—Of these, zircon or hyacinth, $ZrSiO_4$, is the most important. It occurs in crystalline rocks, especially

[1] Moissan, *Compt. Rend.* 1893, **116**, 1,222; 1896, **122**, 651.

in granular limestone, schist, gneiss, syenite, and granite. The chief localities are in alluvial sands in Ceylon, the Urals, in the Isle of Harris, in Greenland, in the gold districts of Australia, and in many places in North America. Zircon crystallises in quadratic prisms and pyramids (Fig. 152), having an adamantine lustre, which in the pure state are colourless. Usually, however, zircon is coloured red or yellow by ferric oxide. The colourless as well as the smoke-coloured variety is termed jargon. This variety exhibits a peculiar absorption spectrum, from which Sorby concluded that it contained a new element to which he gave the name of jargonium, but subsequently he found that these lines were caused by the presence of uranium oxide. An artificial jargon yielded a similar spectrum, though neither uranium nor zirconium compounds do so.[1]

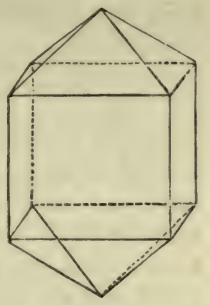


FIG. 152.

DETECTION AND ESTIMATION OF ZIRCONIUM.

357 The reactions of the zirconium salts are very similar to those of the metals contained in cerite and gadolinite. A reaction of zirconium by which it is distinguished from the cerium metals is the formation of a basic potassium zirconium sulphate insoluble in water and hydrochloric acid. This salt is obtained by adding a hot solution of potassium sulphate to a concentrated solution of a zirconium salt. This reaction also serves to separate zirconium from titanium, tantalum, and niobium. Another method of separating zirconium from the metals of the cerium and iron groups is to boil the solution with sodium thiosulphate, when zirconium alone is precipitated as the thiosulphate; this on washing and heating leaves a residue of zirconia.

Titanic acid and thoria are also precipitated together with the zirconia by sodium thiosulphate. In order to separate these, ammonium oxalate is added to the hydrochloric acid solution when the thoria is thrown down. Ammonium carbonate is now added to the filtered liquid when, in the presence of the oxalate, only titanic acid is precipitated, the zirconia remaining in solution (Hermann). Zirconium can readily be separated from iron, titanium, &c., by means of hydrogen peroxide which precipitates

[1] *Chem. News*, 1870, **21**, 73.

it quantitatively from solutions of the sulphate as the hydrated peroxide (Bailey).

The spectrum of zirconium contains the following characteristic lines (Thalén):

6127 in the red.
4815, 4771, 4738, 4709, 4686 in the blue.

Atomic Weight of Zirconium.—The first accurate determination of the atomic weight of zirconium is that of Marignac,[1] who from the analysis of potassium zirconofluoride obtained the number 90·03. Bailey,[2] from the weight of zirconia yielded by a known quantity of pure zirconium sulphate, found the number 89·95, and the atomic weight may therefore be taken as 90·0 (O = 15·88).

TIN (Stannum), Sn = 118·2

358 This metal was known in early times. It is very uncertain whether the word "bedil" in the Old Testament, which is translated by the Greek word *κασσίτερος*, and by the Latin *stannum*, was originally used to designate tin. It is likewise doubtful whether the metal which the Phœnicians are said to have brought from the Cassiterides, whose exact locality was unknown to Herodotus, was really tin. Possibly the Greek word is connected with the Arabic "kasdir," which signifies tin. It is, however, certain that at the beginning of our era the word was used to specify tin, for Pliny states that *cassiteron* and *plumbum candidum* are the same, and he adds that it is more expensive than *plumbum nigrum* (lead); he moreover states that it serves for soldering the latter metal, and that it is obtained from the Cassiterides in the Atlantic Ocean. That the Cassiterides really were the British Islands appears more than probable, for after Cæsar's conquest tin was carried from the Cornish mines through Gaul, by way of Marseilles to Italy;[3] and Diodorus Siculus mentions that the inhabitants carry the tin to a certain island called Iktis, lying on the coast of Britain. "During low water the intermediate space is left dry, and they then carry over abundance of tin to this place in their carts." There can be little doubt that the Iktis of Diodorus is St. Michael's Mount,

[1] *Ann. Chim. Phys.* 1860 (3), **60**, 257.
[2] *Proc. Roy. Soc.* 1890, **46**, 74.
[3] G. Smith, *The Cassiterides.* London, 1863.

in Mount's Bay, in Cornwall; for up to the present day a causeway exists, flooded at high water, but dry at low water, across which the inhabitants are in the habit of carrying goods to and from the mainland. The names by which Pliny designates tin and lead seem, however, to show that he did not consider these as distinct metals, but rather as varieties of one metal, and he adds, "Sequitur naturæ plumbi cujus duo genera, nigrum atque candidum." The word *stannum*, which at a later period became the general designation for tin, also occurs in Pliny's works, though it appears certain that by this word he did not signify tin, but rather any mixture of metals which contains lead. In the works of the Latin Geber the most important properties of tin are mentioned, such as the peculiar crackling sound which the metal emits when bent, as well as the fact that it forms brittle alloys. Tin was termed Hermes by the early Greek alchemists, but about A.D. 500 it received the name of Zeus or Jupiter, and to it the sign ♃ was given; but owing to the above-mentioned property of forming brittle alloys it was sometimes termed, *diabolus metallorum*.

Tin has been found in small quantities in Siberia, Guiana, and Bolivia in the native state, together with metallic gold, though the metallic tin from the last-named locality may, according to Forbes,[1] possibly have been an artificial product.[2] It has also been found in small tablets in bismutite from Mexico.

The chief ore of tin is cassiterite, or tinstone, a more or less pure form of the dioxide, SnO_2. Less frequently it is found as tin-pyrites, $Cu_4SnS_4 + (Fe, Zn)_2SnS_4$, and occasionally as silicate. It also occurs in small quantity in certain epidotes, as well as in columbites, tantalites, and other similar minerals. Various mineral-waters likewise contain traces of tin, and this metal has also been detected in certain meteoric masses.

359 *The Metallurgy of Tin.*—All commercial tin is obtained from tinstone, which is found in veins traversing the older crystalline and schistose rocks. The same is also found as *stream-tin* in water-worn nodules amongst the detritus of the same rocks. Tin ore is not, however, very widely distributed, only occurring in large masses in a few localities. The oldest and best known tin mines from which tin has continuously been obtained, probably from the time of the Phœnicians up to the present, are

[1] *Phil. Mag.* [4], 1865, **29**, 133; **30**, 142.

[2] We have examined the specimen of metallic tin described by Forbes, and are inclined to believe it to be a natural product.

those of Cornwall. The ore there occurs in the granite and in the metamorphic schistose rock, and is found especially rich in the killas, a metamorphic clay slate, and in the line of junction of this with granite. It is found in veins or lodes, in beds or flats, and in ramifications of small veins or "stock werke," and these tin veins usually run in Cornwall in an easterly or westerly direction. The following minerals are frequently found, together with tinstone: wolfram, apatite, topaz, mica, tourmaline, arsenical pyrites, &c.

Tin mines exist, although on a much smaller scale than in Cornwall, in other parts of Europe, as in the Erzgebirge, in Bretagne, and in the Spanish province of Galicia. Very large deposits of tin ores are, however, found in other quarters of the globe. Thus, for instance, in the Island of Banca, and on the Malay Peninsula, large quantities of tin ore are found, chiefly in the form of stream-tin, though it likewise occurs in lodes in granite rocks. This source of tin was discovered at the beginning of last century, and at a later time very rich mines, which are now worked, were discovered in the neighbouring Islands of Bilitong. Tin has also been worked in Bolivia and Peru, and lately very large quantities of tin have been obtained from Australia, and especially from New South Wales and Queensland. In New South Wales the production of tin rose from 47 tons in 1872 to 6,058 tons in 1875,[1] whilst in Queensland a similarly rapid progress was made, but since 1882, the quantity exported from these countries has considerably fallen off. The total world's production of tin from 1891–1895 was as follows:—

1891	59,463 tons
1892	64,569 „
1893	67,077 „
1894	74,307 „
1895	75,333 „

The process adopted in Cornwall for the reduction of the metal is a simple one. The ore, which consists not only of Cornish stone, but likewise of Australian and Peruvian ore, after being stamped, is washed to free it as much as possible from gangue, and is then roasted in calcining furnaces for the purpose of driving off the sulphur and arsenic contained in the arsenical and ordinary pyrites generally mixed with the ore.

[1] *The Industry of New South Wales*, G. H. Reid. Trübner, 1878.

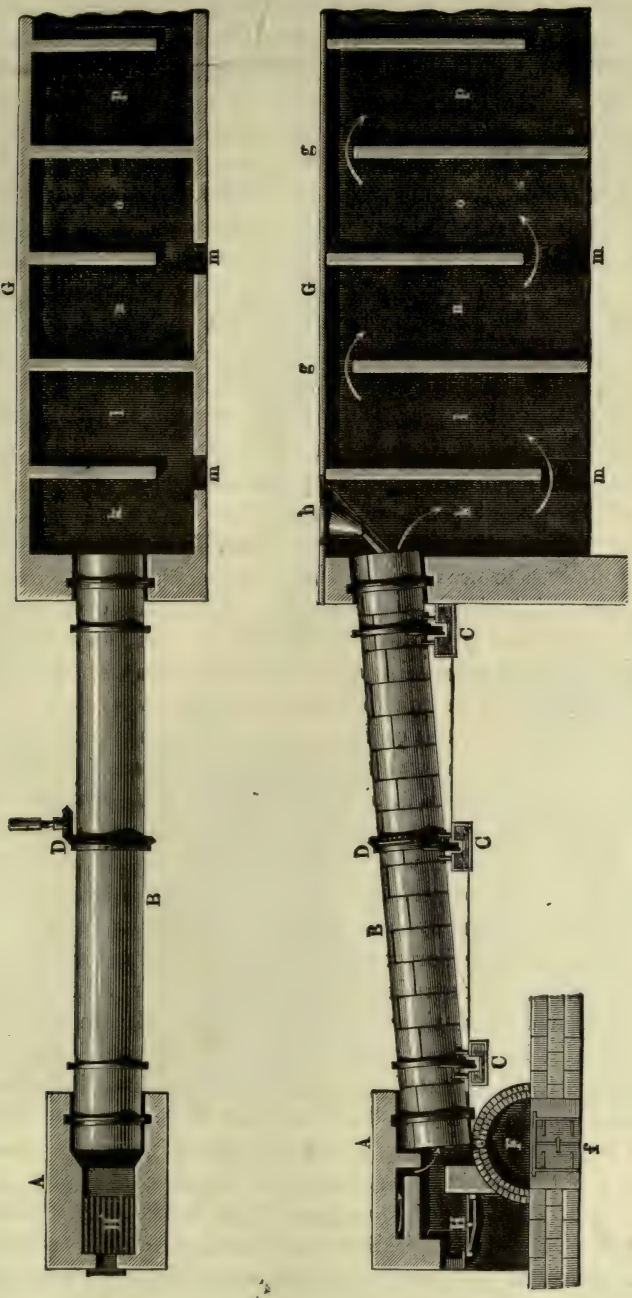


Fig. 153.

The vapours from these revolving calcining furnaces are led into chambers in which the arsenic trioxide condenses. The construction of an Oxland and Hocking's revolving calciner is shown in Fig. 153. This consists of a long cylinder lined with firebrick, and placed in an inclined position. The fire (H) is placed at the lower end (A), whilst the upper end is in connection with chambers in which the arsenious oxide condenses. The ore is dried on the top of these chambers, which are made of iron plate, and then brought by means of the hopper (h) into the cylinder, the roasted ore falling down into the space (F). This then undergoes a second washing in order to remove the ferric oxide and other oxidised materials, and is again roasted for the purpose of volatilising the last traces of arsenic and sulphur. After these operations the roasted ore is found to contain from 60 to 70 per cent. of tin. It sometimes happens that the tin ore is mixed with more or less wolfram, $(Fe, Mn)WO_4$, and as this mineral possesses a high specific gravity, it cannot be removed from the tin ore by washing. In order to remove this impurity, the presence of which in the smelting operations would prove injurious to the quality of the tin obtained, the following process proposed by Oxland is generally adopted. The roasted ore is smelted in a reverberatory furnace with a sufficient quantity of soda-ash to furnish a soluble tungstate of the alkali, together with the oxides of iron and manganese, and the soluble tungstate separated from the oxides of iron and manganese, and the unaltered tinstone by lixiviating with water. The residual roasted ore, or *black tin*, is then mixed with one-fifth part its weight of anthracite and the mixture sprinkled with some water in order to prevent the finely divided ore from being blown by the draft into the chimney. The construction of the reverberatory furnace is shown in Figs. 154 and 155; the charge is introduced by the door (B) on to the hearth (A), and then worked through the door (E). The temperature of the furnace is gradually raised for five hours, the charge then repeatedly stirred, and at the expiration of six hours the reduced metal is tapped and allowed to run from the lower part of the hearth through the hole (f) into the vessel (G). The impure tin thus obtained is then cast into moulds, and these are refined by the process of *liquation*. This is effected by placing the ingots in another similar reverberatory furnace which is gradually heated, so that the pure, more easily fusible tin first melts and runs into a cast-iron vessel (H) placed below, whilst

the less fusible alloy of tin with iron and arsenic remains on the hearth. A fire is placed under the vessel (H) in order to keep the metal liquid, and this is then stirred up with a pole of green

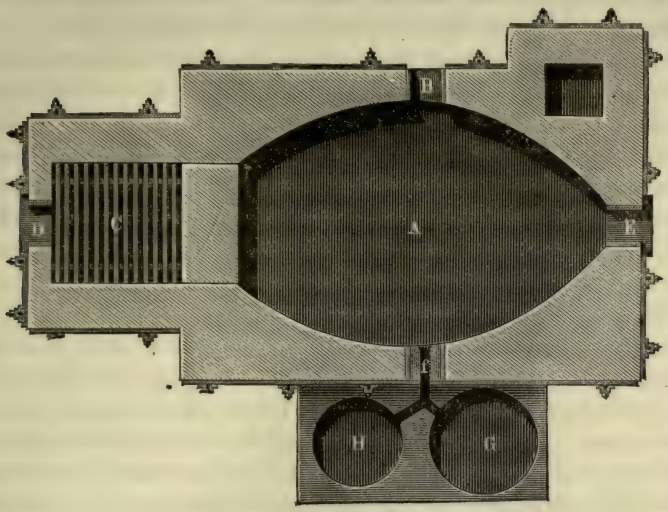


FIG. 154.

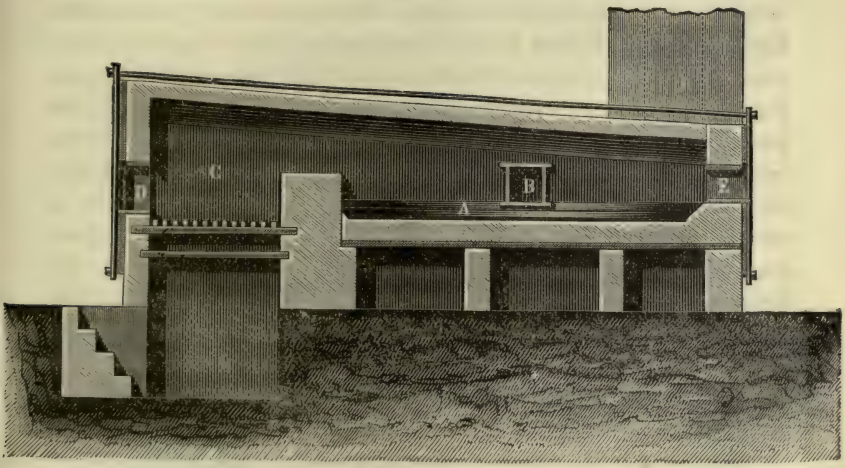


FIG. 155.

wood, usually of an apple-tree. The length of this operation depends upon the quality of the metal which it is desired to obtain, and may last from one to several hours. The dross which separates during the process of refining, and the "hard-

head," or residue which remains on the hearth, both of which contain large quantities of tin, are afterwards worked up. In order to prepare *grain-tin* the block tin is heated until the metal becomes brittle and crystalline; it is then broken up by a hammer, or allowed to fall from a considerable height.

Of the various sorts of commercial tin that from Banca is the purest. It contains only traces of copper, lead, and iron; and for this reason it is usually employed by chemists and manufacturers as the source of the tin salts. Next in order of purity comes English tin. The impurities contained in the common commercial varieties of tin are arsenic, antimony, bismuth, zinc, lead, copper, iron, and less frequently molybdenum, tungsten, and manganese.

360 *Properties and uses of Tin.*—Tin is a white, brightly lustrous metal, which melts at 232° (Heycock and Neville), volatilises between 1450° and 1600° (Carnelley and Williams), and has a specific gravity at 13° of 7·293 (Matthiessen). It is harder than lead, but softer than gold. It exhibits a fibrous fracture, and when bent emits a peculiar crackling sound, caused by the friction of the crystalline particles. Tin can be easily rolled or hammered out to tin-foil, and at a temperature of 100° it may be drawn into wire, which, however, possesses but slight tenacity; but at 200° it becomes so brittle that it may be powdered. A sample of Banca tin which was exposed at St. Petersburg to a very low temperature during the winter, fell to granular crystalline pieces, or to a coarse powder. This alteration of structure may be artificially produced by lowering the temperature of the metal to the freezing point of mercury.[1] If zinc be brought into a solution of tin chloride the metal separates out in the form of fine crystalline dendrites, and this deposit, known as the tin-tree (Arbor Jovis), was first prepared by Ilsemann in 1786. When tin is melted and then allowed partially to solidify, the liquid portion being poured off, needle-shaped prismatic or tabular crystals of the metal remain behind. Another mode of obtaining crystalline tin is to decompose tin chloride by a weak galvanic current when the metal is deposited in quadratic prisms and pyramids. Fine crystals of tin can also be obtained when water containing zinc dust in suspension is gradually added to a solution of tin chloride.

Metallic tin remains bright in dry or moist air at the ordinary temperature, but when melted gradually oxidises forming a

[1] Fritsche, *Ber.* 1869, **2**, 112, 540.

greyish white skin on the surface, which consists of a mixture of tin and stannous oxide and is gradually oxidised to the dioxide. It is dissolved by dilute, and more rapidly by concentrated hydrochloric acid, with evolution of hydrogen and formation of stannous chloride; it also dissolves in aqua regia and in hot concentrated sulphuric acid, and is converted by somewhat diluted nitric acid into metastannic acid. It also dissolves in aqueous solutions of the alkalis, with formation of salts of metastannic acid and evolution of hydrogen.

Tin is used for a large number of purposes, for the preparation of vessels for household and technical use, for the manufacture of tin-foil, for tinning copper and iron, and especially for preparing the alloys of tin. Tinned copper vessels were employed by the ancients, for we find them described by Pliny; and the same author also mentions as a well-known fact, that in the process of tinning, the weight of copper articles increases but slightly, and he adds that the substance termed stannum is employed for this purpose.

Copper- and brass-ware can readily be tinned by dipping the vessel into the molten metal. In order to cover the interior of a vessel with a coating of tin, it is heated and some molten tin poured in, which is then well divided over the surface by rubbing with rags. In order to prevent the oxidation of the metal a small quantity of resin or sal-ammoniac is added. Agricola was the first to mention the process of tinning iron. It appears, however, that at that time it was only slightly employed. The process is usually supposed to have been discovered in Bohemia in 1620, coming into use in England and France about 100 years later. For the purpose of preparing the common tin plate, the iron plate is dipped into hydrochloric acid or dilute sulphuric acid, then rubbed over with sand and water, and lastly dipped into a bath of hot fat, in order to dry and warm it. From this it is brought into a vessel filled with melted tin covered with a film of oil, an alloy of tin and iron being thus formed. This is covered with a film of pure tin by dipping it into a second bath of the metal, and the sheets are lastly dipped into heated tallow in order to remove the excess of tin.

Alloys of Tin.

361 Several of these alloys are largely employed in the arts. Tin and lead may be mixed in any proportion, and the alloy,

termed pewter, is harder and tougher, but more readily fusible than either of the two metals. For this reason it is employed as a solder. The following table gives the composition of some of the different lead and tin alloys:

	Common Pewter.	Solder.		
		Fine.	Common.	Coarse.
Tin . .	4	2	1	1
Lead . .	1	1	1	2

Although the alloys of tin and copper possess a great commercial importance, these metals do not readily unite with one another, and the compound produced is not a stable one; hence the mass seldom remains perfectly homogeneous, though more so than the silver copper alloys. The effect of heat on the copper-tin alloys is remarkable, for whilst steel becomes harder by tempering, these lose their brittleness, and become malleable if they are heated and then plunged into cold water. It is extremely probable that the alloy corresponding in composition to the formula Cu_3Sn is a definite chemical compound[1]; it may be obtained in white crystalline lamellæ by fusing copper with an excess of tin and treating the product with cold concentrated hydrochloric acid. There are indications that the compounds Cu_4Sn and CuSn also exist.

The following are the most important commercial alloys of these metals:—

Gun-metal usually contains nine parts of copper to one of tin, and has a yellow colour. This alloy also serves for the preparation of bronze medals.

Speculum-metal is composed of one part of tin to two parts of copper, melted together, with, frequently, addition of a small quantity of arsenic. It possesses a steel-grey colour, is very brittle, and takes a very high polish.

Bell-metal possesses a varying composition. It generally consists of from 4 to 5 parts of copper to 1 of tin. It has a yellowish-grey colour, and readily melts to form a thin liquid. It has a finely granular structure, is hard, brittle, and very sonorous. The Chinese gongs and tom-toms are cast at a very high temperature, and then quickly brought under the hammer, in consequence of which treatment the alloy becomes very dense.

Bronze. True bronze consists of copper, tin, and sometimes a

[1] Laurie, *Journ. Chem. Soc.* 1888, i. 109; Le Chatelier, *Compt. Rend.* 1895, **120**, 835; Foerster, *Zeit. anorg. Chem.* 1895, **10**, 309.

small quantity of lead. The other metals which are found are impurities, but modern bronze always contains zinc. The colour of bronze is a more or less reddish yellow. It is hard and tough and may be filed and worked in the lathe, whilst in its molten state it forms a mobile liquid.

The table on the next page gives the composition of some of the above described alloys.

Phosphor-bronze. The addition of phosphorus to bronze imparts to it a character of greater hardness, elasticity, and toughness. This material is obtained by melting copper with tin-phosphide with sometimes a small addition of lead. It contains from 0·25 to 2·5 per cent.of phosphorus, and from 5 to 15 per cent. of tin, and is largely used, especially that containing from 7 to 8 per cent. of tin, for portions of machinery for which hardness and toughness are important properties. The alloy containing more tin has been employed for bell-metal. Its valuable properties are connected with the fact that copper forms a homogeneous alloy with tin phosphide, the presence of phosphorus preventing the oxides from dissolving and thus impairing the qualities of the metal.

Tin Amalgam.—Tin readily combines with mercury with diminution of temperature. The amalgam may be formed more quickly when mercury is poured into molten tin, and, according to the quantity of the mercury added, the amalgam is either liquid, or forms a granular or crystalline mass. When mercury is made the negative pole in a solution of tin dichloride, fine crystals of the amalgam are obtained containing from 44 to 51 per cent. of tin (Joule). Tin amalgam is largely used for silvering mirrors. For this purpose tin-foil, which usually contains from 1 to 2 per cent. of copper and a small quantity of lead, is spread out on a perfectly even horizontal slate table. This is then covered with a film of mercury from about 2 to 3 mm. in thickness, and the carefully cleaned sheet of plate glass floated on to its surface, the excess of mercury being pushed forward and the formation of bubbles of air thus guarded against. The glass is then gradually weighted evenly throughout its surface in order to remove the excess of mercury. After the lapse of some time the weights are removed and the plate gradually inclined in order that the excess of liquid amalgam may flow away.

It is not certain when this process for manufacturing mirrors was first employed, inasmuch as, during the middle ages, the processes used in the preparation of mirrors were kept secret.

Analyses of Alloys of Tin.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
Cu .	91·74	67	73·94	82	84·25	87·89	84·53	85·9	70·30	89·43	89·78	88·77	89·34	84·20
Sn .	8·26	33	21·67	17	15·64	10·58	6·82	14·1	24·53	8·17	9·16	9·25	7·50	3·05
Pb .	—	—	1·19	—	—	—	8·65	—	5·20	1·05	1·33	0·71	1·21	0·75
Fe .	—	—	0·17	1	trace	0·27	—	—	—	0·34	—	—	—	—
Zn .	—	—	—	—	—	—	—	—	—	—	2·35	1·28	1·61	11·55
Ni .	—	—	2·11	trace	—	—	—	—	—	0·19	—	—	—	—

I. English gun-metal.
II. Speculum metal used in construction of Lord Rosse's large telescope.
III. Bell cast in 1670 in Darmstadt.
IV. Chinese gong.
V. Egyptian bronze coin of the reign of Ptolemy IX.
VI. Attic bronze coin.
VII. Roman bronze coin of Justinian.
VIII. Gaulish axe.
IX. Celtic arrow-head.
X. Bronze statue of sixteenth century from Augsburg.
XI. Statue of Germanicus, cast in Berlin in 1824.
XII. Thorwaldsen's Shepherd, cast in Berlin in 1825.
XIII. Statue of Bacchus in Berlin, 1830.
XIV. Statue of Lessing in Brunswick.

It is, however, clear that before amalgam was used, a surface of metallic lead was employed for obtaining a mirror as early as the thirteenth century, when such mirrors were common. These were curved, and were prepared, as Beckmann describes in his *History of Inventions*, from large glass globes, into the interior of which a mixture of resin, molten lead, and sulphide of antimony was introduced, the fluid mass being brought over the surface until it was all covered with a thin film. The globe was then cut into pieces, and the mirrors thus obtained were often employed as ornaments. A guild of glass-mirror makers existed at Nuremberg in the year 1373; whether they made mirrors according to the above process is doubtful, but these, as well as French workmen, sold products of their art in the Venetian market up to the year 1500. The use of amalgam for coating mirrors is first mentioned by Kunkel, who recommends for the purpose an amalgam of 2 parts of quicksilver 1 of marcasite (bismuth), ½ part of tin, and ½ part of lead.

COMPOUNDS OF TIN.

Tin and Oxygen.

362 The fact that tin readily forms a calx was observed at an early period. Pelletier was the first, in the year 1792, to show that tin combines in two proportions with oxygen, forming two series of salts. This investigation was continued by Proust, but for a long time considerable doubt existed as to the number of the oxidation products of the metal. Berzelius in 1812 assumed that there were three oxides, SnO, Sn_2O_3, and SnO_2, on the grounds that when the metal is oxidised by nitric acid the highest oxide thus prepared possesses a totally different chemical character from that which is obtained by precipitation with alkalis from a solution of the salts of tin. The subsequent investigations of Davy, Gay-Lussac, and Berzelius himself, proved that only the first and last of these oxides exist. A peroxide, SnO_3, has also been prepared.

Tin Monoxide or *Stannous Oxide*, SnO.—This oxide may be prepared in a variety of ways. In the first place it is obtained as an olive-coloured powder when stannous oxalate is ignited out of contact with air. Secondly, it may be prepared by adding a solution of potassium carbonate to one of tin dichloride, when

a white precipitate, having the composition $Sn_2O(OH)_2$ is thrown down. This readily absorbs oxygen from the air, but if it be washed in absence of air and dried in a stream of carbon dioxide, the monoxide remains behind as a black powder. Stannous oxide is also obtained when the pure dichloride is mixed with sodium carbonate, the mass heated until it has become black, and then lixiviated. If the hydrated oxide be boiled with a dilute solution of caustic potash, the anhydrous oxide is obtained as a crystalline powder, the crystals consisting of combinations of the cube and dodecahedron. It may also be obtained in the crystalline state by digesting a nearly saturated solution of the hydrated oxide in acetic acid at a temperature of 56°.

Stannous oxide readily takes fire when heated in the air, and dissolves in acids with formation of stannous salts, to which it corresponds. These are, however, more readily obtained by the action of acids upon the metal, and possess an unpleasant metallic taste, redden litmus, and readily absorb oxygen, and therefore serve as powerful reducing agents.

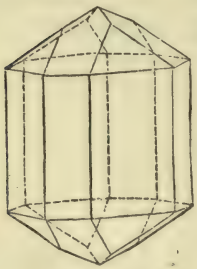


Fig. 156.

Tin Dioxide or *Stannic Oxide*, SnO_2, occurs in nature as tin-stone or cassiterite crystallising in the quadratic system (Fig. 156) and possessing an adamantine lustre. The crystals are seldom colourless, being generally tinted of a brown or black colour from the presence of the oxides of manganese and iron. *Stream-tin* is found in water-worn nodules, and *Wood-tin* in reniform fibrous masses. When tin is heated nearly to its boiling-point in the air, it burns with a luminous white flame, and the dioxide which is thus formed in a state of fine division was formerly known as *flores jovis*. If fused in the presence of air, the surface of the metal soon becomes covered with a grey pellicle, which then passes into a grey powder known as *flores stanni*, and this consists of a mixture of finely-divided metal with the oxide which, on continued ignition, is wholly converted into stannic oxide. The dioxide is also obtained on treating tin with nitric acid, when a violent oxidation occurs. The hydrated white powder thus obtained yields the dioxide on washing and igniting. If a solution of stannic chloride be precipitated with ammonia a gelatinous precipitate is obtained, which can be completely washed only with difficulty. If, however, it be heated with a concentrated solution of an alkali sul-

phate, a dense precipitate is thrown down, and this can be easily washed and yields the pure dioxide on ignition. An amorphous white or straw-yellow coloured powder is then obtained which is quite insoluble in water and possesses a specific gravity of 6·71. On heating it changes colour, becoming lemon-yellow and then brown, but it assumes its original tint on cooling.

By heating amorphous stannic oxide in a current of hydrochloric acid gas it may be obtained in microscopic crystals which have the form of cassiterite and a specific gravity of 6·72 (Deville).[1] The formation of crystallised stannic oxide has been observed in fusing the dross collected on the hearth of a gun-metal furnace. The crystals were hard, brittle, four-sided prisms.[2] Stannic oxide can only be fused at a very high temperature. It is not volatile, nor is it attacked by concentrated acids, with the exception of sulphuric acid; with this it forms a syrupy liquid, from which the crystalline compounds SnO_2,H_2SO_4 and $SnO_2,2H_2SO_4$ may be obtained. The dioxide is deposited from the solution on addition of water.

Stannic Hydroxides.—Two isomeric stannic hydroxides are known, each of which behaves as an acid yielding a corresponding series of salts. From analogy it would be expected that the acids would correspond to meta- and ortho-silicic and titanic acids, and have the composition H_2SnO_3 and H_4SnO_4; as, however, both acids exist in all degrees of hydration between the limits required by these two formulæ,[3] the isomerism must be due to other causes. No satisfactory explanation of the difference in their constitution has, however, as yet been given. The two acids are distinguished as *stannic* and *metastannic acids*, or as *α- and β-stannic acids*, and each yields a series of salts from which the original acid may be again obtained by the action of stronger acids.

Stannic Acid or *α-Stannic Acid* is obtained as a white hydrated precipitate by the action of calcium carbonate on a solution of stannic chloride or bromide, or when a stannate is carefully precipitated with an acid. The well-washed precipitate, which is slightly soluble in water and has an acid reaction, has the composition H_2SnO_3 when dried over sulphuric acid, but if it be obtained by adding a concentrated solution of an alkali sulphate to a solution of stannic chloride and allowed to dry in the air

[1] *Compt. Rend.* 1861, **53**, 161.
[2] Abel, *Journ. Chem. Soc.* 1858, 119.
[3] See Lorenz, *Zeit. anorg. Chem.* 1895, **9**, 376.

it has the composition H_4SnO_4. Both of these gradually lose water on heating, the final product being tin dioxide. Stannic acid dissolves readily in dilute mineral acids as well as in the alkalis. With the latter it yields the alkali stannates which are the only ones soluble in water. The other stannates are obtained as insoluble precipitates by double decomposition.

Potassium Stannate, K_2SnO_3, is obtained by fusing the dioxide with potash or by dissolving the hydrated oxide in potash-ley. The solution yields on evaporation over sulphuric acid colourless glistening monosymmetric prisms of $K_2SnO_3 + 3H_2O$ (Marignac), which have an alkaline taste and are readily soluble in water. Metallic copper brought into contact with the solution becomes covered with a bright coating of tin.

Sodium Stannate, Na_2SnO_3, is prepared on a large scale and employed extensively in calico-printing under the name of *preparing salts*. It is obtained either by fusing the finely-powdered or levigated tin-stone with caustic soda, dissolving the mass in water to remove any ore that may be unacted upon, and evaporating the solution; or by heating tin with caustic soda and Chili saltpetre. On evaporating the solution hexagonal crystals of $Na_2SnO_3 + 3H_2O$ are obtained, which are more soluble in cold than in hot water. A tolerably concentrated solution of the salt which contains no caustic soda deposits on cooling fine prisms of the composition $Na_2SnO_3 + 10H_2O$, and these effloresce on exposure to air.

Metastannic Acid and the Metastannates.—In his *Reflections on the Hypothesis of Alkali and Acidum*,[1] published in 1670, Boyle remarks that aqua-fortis eats up or destroys more tin than it dissolves. On the other hand, he elsewhere[2] mentions that a solution of tin in aqua-fortis readily becomes gelatinous. Kunkel, who also studied the action of nitric acid on tin, mentions in his *Laboratorium Chymicum* that tin can only be dissolved when it is added in small quantities to an acid, and that heat must be altogether avoided, because white calx of tin is thrown down when the acid is hot. The explanation of these different statements is to be found in the facts that when the metal is treated with weak nitric acid it forms either stannous or stannic nitrate according to the degree of concentration of the acid; and that the latter salt easily decomposes with separation of a gelatinous stannic acid,

[1] Boyle, *Op.* **4**, 284.

[2] "Experiments and Considerations Concerning Colours."

whilst on the other hand, when tin is acted upon by strong nitric acid it is violently attacked with evolution of heat and formation of an insoluble white powder consisting of metastannic acid. Metastannic acid reddens litmus, and when dried in the air contains about 20 per cent. of water, which it gradually loses when heated or when dried in a vacuum, during which process, however, no definite hydrate appears to be formed. Metastannic acid is distinguished from ordinary stannic acid, inasmuch as it is altogether insoluble in nitric acid, and swells up but does not dissolve in strong sulphuric acid, forming a compound with it which is decomposed by water. When warmed with concentrated hydrochloric acid it combines with it to form a hydrochloride of metastannic acid, which is insoluble in hydrochloric acid but soluble in water, and which on boiling gelatinises even in very dilute solution.

The salts of metastannic acid are formed by the action of the alkalis on metastannic acid or on its compound with hydrochloric acid. They all possess a very complicated composition and crystallise with difficulty. The sodium salt has been most exactly examined.

Sodium Metastannate, $Na_2Sn_5O_{11} + 4H_2O$, or $H_8Na_2Sn_5O_{15}$.—This is a slightly soluble granular crystalline powder obtained by the action of cold caustic soda-ley on metastannic acid. If a hydrochloric acid solution of metastannic acid be precipitated with caustic soda hard gum-like masses of a compound $Na_2Sn_9O_{19} + 8H_2O$ are obtained.

When solutions of stannic acid in hydrochloric and hydrobromic acid (which are identical with the solutions obtained by the action of water on stannic chloride and bromide) are allowed to stand, the stannic acid slowly undergoes conversion into metastannic acid, which usually separates out as an opalescent precipitate. This change takes place much more rapidly with the hydrobromic than with the hydrochloric acid solution, and may in both cases be followed quantitatively by suitable means.[1] It would therefore appear that the constitution of metastannic acid is more complex than that of stannic acid, and this is confirmed by the fact that many of the metastannates have an even more complicated composition than those mentioned above.

Colloïdal or *Soluble Stannic Acid* was obtained by Graham[2] by the dialysis of a mixture of tin tetrachloride and alkali or of

[1] Lorenz, *Zeit. anorg. Chem.* 1895, **9**, 376.
[2] *Phil. Trans.* 1861, 213.

sodium stannate and hydrochloric acid, the gelatinous mass which is first formed gradually dissolving. The liquid is converted on heating into colloïdal metastannic acid. Traces of hydrochloric acid or of a salt bring about gelatinisation in both solutions.

Tin Trioxide, SnO_3.—This oxide is only known in the hydrated condition, and is prepared by the addition of barium peroxide to a solution of stannous chloride containing hydrochloric acid. The barium chloride is removed by dialysis, and the colloïdal solution evaporated. A white mass having the formula $H_2Sn_2O_7$ or $2SnO_3,H_2O$ remains behind.[1]

Stannous Compounds.

363 *Tin Difluoride* or *Stannous Fluoride*, SnF_2, is obtained by dissolving the hydrated monoxide in hydrofluoric acid. On evaporation in absence of air this compound is obtained in the form of small white monosymmetric tables.

Tin Dichloride or *Stannous Chloride*, $SnCl_2$, is obtained on the large scale by dissolving tin in hydrochloric acid. On evaporating the solution and cooling, crystals of hydrated stannous chloride, $SnCl_2+2H_2O$, known in commerce as *Tin Salt*, separate out in transparent monosymmetric prisms which melt in their water of crystallisation at 40°, and on cooling again yield a crystalline mass. They have a specific gravity of 2·71, and dissolve at the ordinary temperature in 0·37 parts of water. When more strongly heated they partially decompose with evolution of hydrochloric acid, but when dried in a vacuum over sulphuric acid they lose their water. The anhydrous salt, which may also be obtained by heating tin in hydrochloric acid gas, or together with corrosive sublimate, is a transparent mass having a fatty lustre and conchoidal fracture. It fuses at 250° to form an oily liquid which boils at 606°. Its vapour at low temperatures has a specific gravity always less than that required by the formula Sn_2Cl_4, but at a high temperature the value becomes constant agreeing with $SnCl_2$.[2] The hydrated salt dissolves in a small quantity of water with diminution of temperature forming a clear liquid which when diluted with much water becomes turbid, a basic chloride, $2Sn(OH)Cl+H_2O$, being precipitated

[1] Spring, *Bull. Soc. Chim.* 1889 [3], **1**, 180.
[2] Biltz and V. Meyer, *Ber.* 1888, **21**, 22.

and this again dissolves on the addition of acids. The same precipitate is formed when the clear solution is exposed to the action of the air: $3SnCl_2 + H_2O + O = SnCl_4 + 2Sn(OH)Cl$. Stannous chloride also dissolves in alcohol.

Tin Dibromide or *Stannous Bromide*, $SnBr_2$, is obtained when tin is heated in hydrobromic acid gas or distilled with mercuric bromide. It forms a light yellow translucent mass fusing at 215·5°, and soluble in water. A solution of this compound is obtained by acting with hot aqueous hydrobromic acid upon metallic tin.

Tin Di-iodide or *Stannous Iodide*, SnI_2, is best obtained by adding a small excess of iodide of potassium to a warm concentrated solution of stannous chloride. It crystallises in yellowish-red needles which dissolve only slightly in water, though readily in warm solutions of the chlorides and iodides of the alkali-metals, and also in dilute hydrochloric acid. It melts at 316°, solidifying to a crystalline mass which liquefies at a higher temperature. When heated in absence of air it is obtained in the form of a red crystalline mass yielding a scarlet powder.

The fluoride, chloride, bromide, and iodide combine with the corresponding haloid compounds of the alkali-metals and with those of the metals of the alkaline earths to form crystalline double salts.

364 *Tin Monosulphide*, or *Stannous Sulphide*, SnS, is obtained by heating together the metal and sulphur. Thin tinfoil takes fire spontaneously when brought into sulphur vapour. When thus obtained it is a lead-grey tough crystalline mass, which melts at a higher temperature than the metal. When a solution of tin dichloride is saturated with sulphuretted hydrogen, a brown hydrated precipitate is obtained, which on drying becomes black. This is scarcely soluble in ammonium sulphide, but dissolves on the addition of sulphur, and is also soluble in the polysulphides of the alkali-metals, the stannous sulphide being first converted by the sulphur into stannic sulphide, which then dissolves forming ammonium thiostannate. When the dried precipitate is added to fused stannous chloride and the melted mass treated on cooling with dilute hydrochloric acid, stannous sulphide is obtained in metallic glistening crystalline scales, having a specific gravity of 4·973. Amorphous tin sulphide dissolves readily in hot hydrochloric acid; the crystallised substance dissolves less readily.

Stannous Sulphate, $SnSO_4$, is formed by dissolving the metal

or the hydrated oxide in dilute sulphuric acid. On evaporation in a vacuum microscopic granular crystals are obtained which are only a little more soluble in hot than in cold water. The solution readily deposits a basic salt.

Stannous Nitrate, $Sn(NO_3)_2$.—This salt is obtained by the action of very dilute nitric acid on the metal, ammonium nitrate being simultaneously produced:

$$4Sn+10HNO_3=4Sn(NO_3)_2+NH_4NO_3+3H_2O.$$

Stannic Compounds.

365 *Tin Tetrafluoride*, or *Stannic Fluoride*, SnF_4, is only known in aqueous solution, this being obtained by dissolving the hydrated dioxide in hydrofluoric acid; the solution coagulates on boiling and decomposes on evaporation with evolution of hydrofluoric acid. It combines with other fluorides forming a characteristic series of double salts termed the *stannofluorides*, which mostly crystallise well and are isomorphous with the corresponding silicofluorides, titanofluorides, germanofluorides, and zirconofluorides.[1]

Potassium Stannofluoride, $K_2SnF_6+H_2O$, is obtained by neutralising hydrofluoric acid with potassium stannate. It crystallises in thin nacreous tablets, or in rhombic pyramids, which are much more soluble in hot than in cold water. When the solution contains an excess of hydrofluoric acid, the salt $K_2SnF_6+HKF_2$ is deposited in thin monosymmetric prisms.

Sodium Stannofluoride, Na_2SnF_6, forms glistening crystalline crusts.

Ammonium Stannofluoride, $(NH_4)_2SnF_6$, crystallises in rhombohedra, which are seldom perfect. Fine rhombic prisms of the compound $(NH_4)_2SnF_6+2NH_4F$ are deposited from a solution containing an excess of ammonium fluoride.

The stannofluorides of calcium and magnesium are also crystalline soluble salts.

Tin Tetrachloride, or *Stannic Chloride*, $SnCl_4$, was first mentioned by Libavius in 1605, who obtained it by distilling tin or its amalgam with corrosive sublimate. It was termed by him *Spiritus argenti vivi sublimati*, but afterwards it received the name *Spiritus fumans Libavii*. For its preparation

[1] Marignac, *Ann. des Mines*, 1859 (5), **15**, 221.

the process originally proposed by Libavius may be employed, or chlorine may be passed over tinfoil or fused tin placed in a retort. When the stream of chlorine is quick, and especially if the gas-delivery tube dip into the molten metal, an evolution of light and heat is observed. Tin tetrachloride is a colourless thin, fuming liquid, which solidifies at $-33°$, has a specific gravity of 2·234 at 15°, and boils at 113·9°,[1] forming a colourless vapour having the normal specific gravity of 9·1997 (Dumas). At the boiling-point it dissolves rhombic sulphur, colourless phosphorus, and iodine, and can be mixed in all proportions with bromine and carbon bisulphide. When mixed with turpentine so much heat is evolved that the hydrocarbon takes fire. Its property of fuming in the air depends on the fact that it absorbs atmospheric moisture. In 1770 Demachy observed that it solidifies when brought into contact with one-third of its weight of water to form a crystalline mass, termed *butter of tin*. Several distinct hydrates soluble in water may be produced, according to the quantity of water which is added. Thus the compound $SnCl_4+3H_2O$ is formed by exposing the anhydrous chloride to the action of moist air, or by the evaporation of its aqueous solution. This hydrate crystallises in monosymmetric needles which melt at 80°, and on cooling again solidify to a crystalline mass. A second hydrate, having the composition $SnCl_4+5H_2O$, is obtained by the addition of a sufficient quantity of water to the anhydrous chloride or by the gentle evaporation of the aqueous solution. It is deposited in opaque, acute, monosymmetric prisms, which melt at a low temperature and again solidify to a crystalline mass. Lastly, large transparent monosymmetric crystals of the hydrate $SnCl_4+8H_2O$ are deposited in the cold from dilute solution. On boiling a dilute aqueous solution of tin tetrachloride, stannic hydroxide is formed, and in very dilute solutions this precipitate forms spontaneously on standing.

Tin tetrachloride is employed by the dyer as a valuable mordant. Drebbel in Holland is said to have made the discovery that by help of this salt a permanent red dye can be obtained from cochineal. The dyers were formerly in the habit of preparing this mordant, known by the old names of tin-composition, physic, or dyer's spirits, by dissolving tin, together with sal-ammoniac or common salt, in nitric acid, or by dissolving tin in aqua regia, whence the solution was formerly termed nitro-

[1] Thorpe, *Journ. Chem. Soc.* 1880, i. 331.

muriate of tin. It is usual now for the dyers to employ the crystalline pentahydrate, $SnCl_4+5H_2O$, which is a commercial product known as *oxymuriate of tin.*

Anhydrous stannic chloride combines with ammonia to form a solid mass having the composition $SnCl_4(NH_3)_4$ (Persoz),[1] which can be sublimed and is soluble in water without decomposition. It can be obtained in crystals by evaporating the aqueous solution over sulphuric acid, but if it be allowed to stand for some days, or if the liquid be warmed, stannic hydroxide separates out in a gelatinous form. Tin tetrachloride also combines with many other chlorides to form crystalline compounds,[2] such as $SnCl_4+2SCl_4$. This is obtained by the action of chlorine on tin disulphide, and forms large yellow crystals, which melt at a summer temperature, and decompose above 40°, with evolution of chlorine. If dry nitrous fumes be led into a solution of stannic chloride, the compound $SnCl_4+N_2O_3$ is deposited as a yellow amorphous mass, and if this be sublimed, or if the dry vapours from aqua regia be passed into the chloride, the compound $SnCl_4+2NOCl$ is produced, which crystallises in bright shining octohedra. Stannic chloride also combines with phosphorus pentachloride to form the compound $SnCl_4+PCl_5$, which sublimes in glistening colourless crystals, but when kept even in closed vessels it falls to an amorphous powder. It has a peculiar extremely pungent smell, and fumes strongly in the air. The compound $SnCl_4+POCl_3$ forms crystals which melt at 58° and can be distilled at 180° without decomposition. This compound fumes strongly in the air, and is at once decomposed in contact with water.[3]

Like the fluorides stannic chloride readily yields a series of double salts known as the stannochlorides. The free acid, H_2SnCl_6, is obtained in thin plates containing 6 molecules of water by saturating the pentahydrate, $SnCl_4+5H_2O$, with hydrochloric acid gas at 28° and cooling the resulting liquid to 0°.[4]

Ammonium Stannochloride, $(NH_4)_2SnCl_6$, separates as a crystalline powder when solutions of the two salts are mixed, and crystallises from dilute solution in small regular octohedra. It dissolves at the ordinary temperature in three parts of water. Its concentrated solution can be boiled without decomposition, but when diluted, tin hydroxide separates out. It was formerly

[1] *Ann. Chim. Phys.* 1830, **44**, 322.
[2] H. Rose, *Pogg. Ann.* 1837, **42**, 517.
[3] Casselmann, *Annalen*, 1852, **83**, 257.
[4] Engel, *Compt. Rend.* 1886, **103**, 213; Seubert, *Ber.* 1887, **20**, 793.

much used by the calico-printer under the name of *pink-salt* from its power of acting as a mordant for madder-red colours, but its use has been almost entirely superseded by the crystalline pentahydrated stannic chloride.

Tin Tetrabromide, or *Stannic Bromide*, $SnBr_4$.—Tin and bromine unite together with evolution of light and heat. The action is moderated by adding the metal gradually to a solution of bromine in carbon bisulphide. It is best prepared by adding bromine very slowly to strips of tin, the temperature being kept between 35 and 59°.[1] This compound is a white crystalline mass, which fumes strongly on exposure to air and is easily soluble in water. It melts at 33° and boils at 201°. The specific gravity of the liquid is 3·349 at 35°, and its vapour density is 7·92.[2] It is easily soluble in cold water, forming a colourless liquid from which the hydroxide is deposited slowly on standing at the ordinary temperature and quickly on boiling. It yields crystalline stannobromides with the alkali bromides.

Tin Tetra-iodide, SnI_4.—When tin and iodine are heated together, combination commences at 50°, and at a higher temperature heat and light are emitted. In order to prepare this compound, tin filings are first moistened with carbon bisulphide and then iodine gradually added. It crystallises in red octohedra, melting at 146° and having a specific gravity of 4·696. Tin tetra-iodide boils at 295°, but sublimes at as low a temperature as 180° in yellowish-red needles, very similar in form to those of sal-ammoniac. It is soluble in carbon bisulphide, absolute alcohol, ether, chloroform, and benzene, and is decomposed by water into hydriodic acid and stannic oxide.

Tin Disulphide, or *Stannic Sulphide*, SnS_2.—This compound, crystallising in six-sided tablets or in gold-coloured translucent scales having a specific gravity of 4·425, is used as a bronze-powder for the purpose of bronzing articles of gypsum, wood, &c., and is known in commerce as mosaic gold. The discovery of this compound is usually ascribed to Kunkel. He does indeed speak of a sublimation of sulphide of tin and sal-ammoniac, but expresses himself so vaguely that it is impossible to recognise this compound from his description. It was well known in the eighteenth century under the names of mosaic gold, *aurum mosaicum*, or *musirum*. It was then prepared as it is at the present day by subliming a mixture of tin amalgam,

[1] Lorenz, *Zeit. anorg. Chem.* 1895, **9**, 365.

[2] Carnelley and O'Shea, *Journ. Chem. Soc.* 1878, i. 55.

sulphur, and sal-ammoniac, and as it was supposed to contain mercury it was often employed as a mercurial medicine. Peter Woulfe in 1771 showed that it did not contain mercury, and described other methods for its production acccording to which it is still prepared. Thus, for instance, it is obtained in the form of a fine pigment by heating eighteen parts of tin amalgam containing six parts of mercury with six parts of sal-ammoniac and seven parts of sulphur, when sal-ammoniac, mercuric chloride, and stannous chloride sublime and stannic sulphide remains behind in the form of golden-yellow scales. It is likewise prepared by heating tin monosulphide with eight parts of corrosive sublimate, or subliming tin filings with sal-ammoniac and sulphur, and according to several other receipts given by Woulfe.[1] Pelletier believed mosaic gold to be a compound of sulphur with the highest oxidation product of tin, and Proust, who found that it could be obtained by heating stannous chloride or tin monoxide with sulphur, supposed it to be a compound of tin, sulphur, and a small quantity of oxygen. The exact composition was ascertained by J. Davy and Berzelius in the year 1812. The formation of mosaic gold from tin, sulphur, and sal-ammoniac, appears to take place according to the following equations (Gmelin):

(I.) $Sn+4NH_4Cl=(NH_4Cl)_2SnCl_2+H_2+2NH_3$
(II.) $2(NH_4Cl)_2SnCl_2+S_2=SnS_2+2NH_4Cl+(NH_4Cl)_2SnCl_4$.

When heated, a portion sublimes without decomposition, but the greater part is resolved into sulphur and monosulphide. It is not attacked by hydrochloric or nitric acid, but readily dissolves in aqua regia, as well as in caustic potash, when potassium stannate and potassium thiostannate are formed. If sulphuretted hydrogen be led into a solution of the tetrachloride a yellow precipitate is obtained. This consists of a mixture of tin disulphide and tin dioxide, and is readily soluble in the sulphides of the alkali-metals, when the *thiostannates* are formed.

Thiostannic Acid.—When dilute hydrochloric acid is added to a solution of a thiostannate, a yellow precipitate is obtained, which on drying forms an almost black powder possessing a brown streak and wax-like lustre, and having the composition H_2SnS_3. When heated in absence of air it yields the golden-yellow disulphide.[2]

[1] *Phil. Trans.* 1771, 114.
[2] Kühn, *Annalen*, 1852, **84**, 110.

Potassium Thiostannate, $K_2SnS_3 + 3H_2O$, is prepared by boiling a concentrated solution of potassium sulphide with the necessary quantities of sulphur and tin. It crystallises in colourless prisms; by a similar process the sodium salt, $Na_2SnS_3 + 2H_2O$, is obtained in yellow vitreous regular octohedra.[1] When sodium sulphide is fused together with tin monosulphide and sulphur, a black crystalline mass is obtained yielding a dark-coloured solution, which on concentration at a low temperature yields colourless crystals resembling gypsum, and having the formula $Na_4SnS_4 + 12H_2O$.

When mosaic gold is fused with iodine in absence of air, a crystalline mass of SnS_2I_4 is obtained, and this can be sublimed in a current of carbon dioxide in dark-yellow glistening crystals, and may be recrystallised from solution in carbon bisulphide, when large crystals, having the colour of potassium dichromate, are obtained. It is decomposed slowly by cold, but more rapidly by hot water, into stannic oxide, sulphur, and hydriodic acid.

Stannic Oxysulphide, $Sn_2OS_3 + 11H_2O$.—This compound is obtained by allowing precipitated stannic sulphide to remain in contact with ammonia, filtering and acidifying the filtrate, or by digesting the sulphide with ammonium carbonate and acidifying the filtered solution. It is a white mass which is soluble in ammonia and gradually becomes yellow on keeping.[2]

Stannic Sulphate, $Sn(SO_4)_2$.—As already mentioned tin dioxide dissolves in concentrated sulphuric acid, and from the solution two crystalline bodies may be obtained having the empirical formulæ $SnO_2,2H_2SO_4$ and SnO_2,H_2SO_4, which may be regarded as the normal sulphate, $Sn(SO_4)_2 + 2H_2O$, and the basic sulphate, $Sn(SO_4)_2,SnO_2 + 2H_2O$. Both of these are decomposed by water with separation of stannic oxide.

Stannic Nitrate, $Sn(NO_3)_4$, is obtained as a white powder by the action of 70 per cent. nitric acid on tin, but must be quickly removed, as it is rapidly converted into the hydrated dioxide. It is a white substance which is stable in presence of concentrated nitric acid at 90°, but is immediately decomposed at 100°.[3] It dissolves in water, but the solution is almost immediately decomposed with separation of hydrated stannic oxide.

Tin and Phosphorus.—When finely-divided tin is heated in

[1] Ditte, *Compt. Rend.* 1882, **95**, 641.
[2] Schmidt, *Ber.* 1894, **27**, 2739.
[3] Montemartini, *Gazzetta*, 1892, **22**, 384.

the vapour of phosphorus, a silver-white very brittle mass, having the composition SnP, is obtained. This has a specific gravity of 6·56, and dissolves easily in hydrochloric acid, but is not attacked by nitric acid. When phosphorus is thrown on to the surface of molten tin, combination also takes place. The compound containing the largest quantity of phosphorus which can thus be obtained has a silver-white colour, is not very brittle, and may be cut with a knife; it appears to possess the composition Sn_3P_2 (Pelletier). If spongy tin, obtained by precipitating a tin salt with zinc, be brought into contact with such a quantity of phosphorus that one atom of the latter be present to nine atoms of the metal, a phosphide having the composition Sn_9P is obtained. The same compound is formed whenever any of the other phosphides containing more phosphorus are heated. This is a coarse crystalline mass, which has the appearance of cast-zinc. It melts at 370°, and is used for the preparation of phosphor-bronze.

Stannic Pyro-phosphate is obtained by the action of phosphoric acid on stannic acid, and is insoluble in water and in nitric acid. This reaction is employed for the separation of phosphoric acid from other bodies. For this purpose a known quantity of tinfoil is added to the nitric acid solution of the body under investigation, when the whole of the phosphoric acid remains behind with the metastannic acid.

Detection and Estimation of Tin.

366 When a small quantity of a tin compound is held in the reduction-flame on a carbonised match, a malleable bead of metal is obtained, which easily dissolves in hot hydrochloric acid. This solution gives with a small quantity of mercuric chloride a white precipitate which becomes grey on boiling:

$$\text{(I.)}\ SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$
$$\text{(II.)}\ SnCl_2 + 2HgCl = SnCl_4 + 2Hg.$$

If one of the metallic globules be fused in a borax bead slightly tinted with cupric oxide and heated in the reduction-flame, the bead will become of a red tint, due to the formation of cuprous oxide.

Stannous salts yield a brown precipitate of stannous sulphide with sulphuretted hydrogen, which does not dissolve in pure

ammonium sulphide solution; if, however, the latter contains polysulphides, these convert the stannous into stannic sulphide, which at once dissolves, forming ammonium thiostannate; the solution, on addition of an acid, deposits stannic sulphide Ammonia and caustic alkalis give a white precipitate of stannous hydroxide, which is soluble in an excess of the latter reagents.

Stannic salts yield a yellow precipitate of stannic sulphide with sulphuretted hydrogen, readily soluble in ammonium sulphide, and alkalis precipitate stannic hydroxide, which dissolves in an excess of the precipitant.

Zinc precipitates metallic tin from solutions of the tin salts in the form of glistening scales or in a spongy or arborescent mass. The tin salts do not impart to the non-luminous gas-flame any colour, but the spark-spectrum of the chloride exhibits two characteristic lines, having wave-lengths of 4526 and 5631 (Lecoq de Boisbaudran). These same lines are seen together with others in the spark-spectrum of the metal, the most brilliant of the tin lines being as follows (Thalén):

6452	5631	5563
5798	5588	4526

In the processes of qualitative analysis tin is obtained together with those metals which are precipitated by sulphuretted hydrogen in an acid solution. To separate tin from these the well-washed precipitate is treated with yellow sulphide of ammonium, filtered, and the filtrate acidified with cold dilute hydrochloric acid. The precipitate may contain, besides stannic sulphide, the sulphides of arsenic and antimony. After it has been well washed with water, it is digested with solid ammonium carbonate to dissolve the sulphide of arsenic. The residue is then dissolved in concentrated boiling hydrochloric acid, the solution boiled with metallic copper, and the liquid tested for stannous chloride with mercuric chloride.

Tin is determined *quantitatively* as the oxide. If the metal or one of its alloys be under examination, it is oxidised with pure, tolerably strong nitric acid, and the well-washed residue ignited. From solution it is precipitated with ammonia as the hydroxide, but if it be present in the form of stannous salt it must be first oxidised with chlorine or hydrochloric acid and potassium chlorate. The precipitate obtained by ammonia is then dissolved in the smallest quantity of hydrochloric acid, and

heated with a concentrated solution of sodium sulphate, when the hydroxide is again precipitated, and this is not gelatinous, and may therefore be easily washed (Löwenthal). When tin sulphide is obtained in the separation of tin from the other metals, it can be gradually converted by gentle roasting and subsequent ignition into stannic oxide.

Atomic Weight of Tin.—The early determinations of the atomic weight of tin were made by oxidising the metal to the dioxide, but the numbers obtained varied considerably. Thus Berzelius found the number 116·85, and Mulder and Vlandeeren 115·4, whilst a later determination by the last-named gave the higher value 117·27. Dumas by the same method obtained the number 117·18, whilst the estimation of the chlorine in stannic chloride gave the number 117·23. The most reliable determination is, however, that of Bongartz and Classen,[1] who employed four different methods, namely the oxidation of pure tin with nitric acid, and the electrolysis of potassium stannochloride, ammonium stannochloride, and stannic bromide. The average of the most trustworthy experiments gave the number 118·2 (O = 15·88).

CERIUM. Ce = 139.

367 The sources of this metal, which always occurs along with the rare earths, have already been mentioned in describing the latter, as well as the means by which it is separated (p. 626). The metal itself was first prepared by Mosander in the form of powder, by heating the chloride with sodium. Wöhler afterwards obtained it in the coherent state, and Hillebrand and Norton have prepared it in large quantity by the electrolysis of the chloride, whilst Winkler prepared it by heating the dioxide with magnesium powder; it possesses the colour and lustre of iron, and is tolerably permanent in dry air, but in moist air tarnishes, becoming first of a yellow, then of a blue, and finally of a green colour. It possesses the hardness of calc-spar, and can be hammered and rolled, and, when warm, drawn into wire. The electrolytically prepared metal has a specific gravity of 6·628, but after melting under common salt it has a specific gravity of 6·728. Cerium melts at a lower

[1] *Ber.* 1888, **21**, 2900.

temperature than silver, but at a higher one than antimony. It takes fire more easily than magnesium, and when scratched with a wire, or scraped with a knife the particles of finely-divided metal which are rubbed off take fire. The same phenomenon is observed when the metal is struck with a piece of flint, sparks of the metal flying off and burning with great brilliancy. The metal also burns in the flame with a much more brilliant light than magnesium. It reacts with the elements of the chlorine group, water, and acids in a similar way to lanthanum, but it is not attacked in the cold by concentrated nitric acid.

According to Schützenberger[1] and Brauner[2] the cerium compounds prepared from cerite invariably contain small quantities of the derivatives of an element of lower atomic weight, the complete separation of which has probably not yet been effected.

CERIUM COMPOUNDS.

Cerium and Oxygen.

368 Cerium forms three oxides: (1) a sesquioxide, Ce_2O_3; (2) a dioxide, CeO_2, and (3) a peroxide, CeO_3. The first two are basic oxides, and yield corresponding series of salts known as the *cerous* and *ceric* salts, but the dioxide, like the corresponding lead compound, acts in many respects as a peroxide.

Cerium Sesquioxide, Ce_2O_3, is obtained as a bluish-green powder by heating the oxalate or carbonate in a current of hydrogen gas. When caustic soda is added to its salts, a white voluminous precipitate of the hydroxide is thrown down. This on exposure to the air takes up oxygen and carbon dioxide, and becomes coloured yellow. Its specific gravity is 6·937.

Cerium Dioxide, CeO_2, is formed when a cerium salt of a volatile oxyacid is heated in the air, and is thus obtained as a white or pale straw coloured powder, which assumes a reddish tinge on ignition, and has a specific gravity of 6·739. If obtained by the ignition of the hydrated oxide it has a salmon colour. It may be obtained in the crystalline form by igniting cerous chloride with borax in a wind furnace.[3] It dissolves in

[1] *Compt. Rend.* 1895, **120**, 663; 962.
[2] *Chem. News*, 1895, **71**, 283.
[3] Nordenskiöld, *Pogg. Ann.* 1861, **114**, 612.

concentrated sulphuric acid forming a dark yellow solution which has powerful oxidising properties, and evolves considerable quantities of ozonised oxygen.

When the acid sulphate is heated with caustic potash or when chlorine acts on the hydrated sesquioxide suspended in water, the hydrated dioxide, $CeO_2 + 3H_2O$, is formed as a sulphur-yellow powder, whilst, if the hydroxide precipitated by the action of ammonia on a solution of cerium sulphate is dried at 385°, a bright yellow hydroxide, $CeO_2 + 2H_2O$ or $Ce(OH)_4$, is obtained, which does not lose water to any considerable extent until heated to 600°.[1] The hydroxides dissolve in hydrochloric acid yielding a deep yellow solution which on heating yields the trichloride, chlorine being simultaneously evolved. The dioxide behaves therefore both as a basic oxide and a peroxide. A higher hydrated *peroxide*, $CeO_3 + nH_2O$, is also known.[2]

Cerous Salts.

369 *Cerous Chloride*, $CeCl_3$, is formed as a yellowish-white sublimate when the metal is heated in chlorine, or when an intimate mixture of the oxide and carbon is heated in this gas. The hydrated salt, $2CeCl_3 + 15H_2O$, remains behind in ill-defined crystals when a solution of cerous oxide in hydrochloric acid is allowed to evaporate over sulphuric acid, and the hydrate, $CeCl_3 + 7H_2O$, has also been obtained in rhombic crystals. On heating, it decomposes with evolution of hydrochloric acid and formation of a basic chloride.

Cerous Bromide, $2CeBr_3 + 3H_2O$, forms deliquescent needles which, when heated in the air, decompose with evolution of bromine.

Cerous Iodide, $CeI_3 + 9H_2O$, forms transparent easily soluble crystals, which readily decompose with evolution of iodine.

Cerous Sulphide, Ce_2S_3, is formed when the metal is burnt in the vapour of sulphur or when the oxide is heated in carbon bisulphide vapour. When the oxide is fused with three parts of sodium pentasulphide, and the fused mass lixiviated with water, cerium sulphide is obtained in small crystals resembling Mosaic gold, which do not undergo alteration on exposure to the air.

Cerous Sulphate, $Ce_2(SO_4)_3$, dissolves in 1·7 parts of cold, and about 60 parts of hot water.[3] When the solution is evaporated

[1] Carnelley and Walker, *Journ. Chem. Soc.* 1888, i. 84.
[2] De Boisbaudran, *Compt. Rend.* 1885, **100**, 605.
[3] Jolin, *Bull. Soc. Chim.* 1874, **21**, 536.

at a moderate temperature the salt $Ce_2(SO_4)_3 + 6H_2O$ crystallises out. Other hydrates are also known.

Potassium Cerous Sulphate, $3K_2SO_4 + Ce_2(SO_4)_3$, is formed when an equal or greater weight of potassium sulphate is added to a solution of cerous sulphate. It dissolves in about fifty-six parts of water at 20°, and is almost insoluble in a concentrated solution of potassium sulphate. It dissolves, however, readily in acidified water, and on slow evaporation a double salt, $Ce_2(SO_4)_3 + 2K_2SO_4 + 3H_2O$, crystallises out. If less than the above proportion of potassium sulphate be added to a solution of cerous sulphate, another salt having the composition $Ce_2(SO_4)_3 + K_2SO_4$ is formed as a granular crystalline mass.

Sodium and ammonium sulphate also form with cerium sparingly soluble double salts.

Cerous Nitrate, $Ce(NO_3)_3 + 6H_2O$, is a crystalline mass which begins to decompose about 200°. It is easily soluble in water and in alcohol, and forms crystalline double salts with other nitrates.

Cerous Phosphate, $CePO_4$, occurs in the mineral monazite $(CeLaDi)PO_4$. This mineral often contains thorium, tin, manganese, and calcium in varying quantities. It crystallises in brownish hyacinth-red monosymmetric crystals, and occurs in the Urals, in Norway, and in several localities in the United States.

Cerous Carbonate, $Ce_2(CO_3)_3$, occurs in lanthanite, and may be obtained by precipitating a solution of cerous sulphate with ammonium carbonate. The precipitate thus obtained has the composition $Ce_2(CO_3)_3 + 5H_2O$, and on standing assumes the form of small silky needles.

Ceric Salts.

370 *Ceric Fluoride*, $CeF_4 + H_2O$, is obtained by acting on hydrated cerium dioxide with hydrofluoric acid, and on heating yields water and then hydrofluoric acid and free fluorine.[1]

Ceric Sulphate, $Ce(SO_4)_2 + 4H_2O$, is obtained by dissolving the dioxide in dilute sulphuric acid and evaporating the salt in a vacuum over sulphuric acid. It is then deposited in the form of reniform masses consisting of fine crystals. In the moist state these are brown, whilst when dried they are yellow. When an excess of concentrated sulphuric acid is poured on the dioxide

[1] Brauner, *Monatsh.* 1882, **3**, 8.

and the solution, diluted with water, gradually allowed to evaporate, the salt $Ce_2(SO_4)_3 + 2Ce(SO_4)_2 + 24H_2O$ is deposited in fine red hexagonal crystals, whilst from the mother liquor yellow crystals of $Ce(SO_4)_2 + 4H_2O$ are deposited.

Ceric sulphate forms double sulphates with the sulphates of the alkali-metals, such as $Ce(SO_4)_2 + 2K_2SO_4 + 2H_2O$, a compound which is deposited in small yellow monosymmetric crystals. Ceric sulphate is decomposed by water with formation of basic salts, from which water extracts more and more acid, and thus, according to the quantity of water present, salts possessing different compositions can be obtained.

Ceric Nitrate is formed by dissolving the hydrated dioxide in nitric acid. The red solution is decomposed by water, with separation of a basic salt. If potassium nitrate be added to the acid solution, and the liquid allowed to crystallise in a vacuum over lime, yellow glistening six-sided prisms are deposited, having the composition $2Ce(NO_3)_4 + 2KNO_3 + 3H_2O$. Ceric nitrate also forms double salts with other nitrates.

Ceric Carbide, CeC_2, is obtained by heating cerium dioxide with sugar charcoal in the electric furnace, and forms a reddish-yellow transparent crystalline substance. On treatment with water it yields a mixture of 75 per cent. of acetylene, 4 per cent. of ethylene and 21 per cent. of methane.[1]

Detection and Estimation of Cerium.

371 The spark-spectrum of cerium contains a number of bright lines, of which the brightest and most characteristic lie in the green and blue. A characteristic reaction for the cerium compounds is the precipitation of red ceric hydroxide when sodium hypochlorite is added to a colourless cerous salt; this dissolves in warm hydrochloric acid with evolution of chlorine. The other reactions have already been described.

In order to determine cerium quantitatively the solution is precipitated with caustic potash, and the washed and dried precipitate heated in the air in order to convert it into the dioxide.

The *atomic weight* of cerium has been determined by several chemists. Bunsen[2] and Rammelsberg[3] found the number 137,

[1] Moissan, *Compt. Rend.* 1896, **122**, 357.
[2] *Annalen*, 1853, **86**, 265; 1858, **105**, 40.
[3] *Pogg. Ann.* 1859, **108**, 40.

and Brauner[1] and Robinson[2] the number 139·2. Still more recently Brauner[3] by the analysis of cerium oxalate obtained the numbers 139·2, 139·0 and 139·3 (O = 15·88).

LEAD.

Pb (Plumbum) = 204·85.

372 The first mention of lead occurs in the well-known passage in the Book of Job, and it is also mentioned in the Book of Numbers as a portion of the spoil taken from the Midianites. It is found under the name of óphéret, derived from the word áphár, signifying to have a grey appearance. In the oldest Greek translations of the Old Testament the word μόλιβος occurs, and this as well as the word μόλυβδος undoubtedly refers to lead. It appears that no exact distinction was drawn between the metals lead and tin during the time of the Israelites, but we find that Pliny points out a distinction between these two metals, inasmuch as he gives the name of *plumbum nigrum* to lead, whilst tin is designated as *plumbum candidum* (p. 662).

It has already been stated that the seven metals known to the ancients were supposed to be in some way connected with the seven heavenly bodies which were then known to belong to our solar system. Dull, heavy lead was apportioned to Saturn; and this metal is designated in the writings of the alchemists by the sign ♄.

Lead is seldom found in the free state in nature. Native lead does, however, occur in small quantities in certain lead ores, and in volcanic tufa. The oxides of lead are found in the form of rare minerals, the yellow oxide PbO, and the red oxide or red lead, Pb_3O_4. The commonest ore of lead is galena or lead sulphide, PbS; this is very widely distributed, generally occurring together with quartz, calc-spar, fluor-spar, and heavy-spar in the older as well as in the more recent strata and in almost every part of the world. Thus in Cornwall it occurs in veins in the coarse argillaceous schist, provincially termed killas; in Derbyshire, Cumberland, Northumberland, and Yorkshire, it is found in mountain limestone; in Cardiganshire and Mont-

[1] *Journ. Chem. Soc.* 1885, i. 879. [2] *Proc. Roy. Soc.* 1884, **37**, 150.
[3] *Chem. News*, 1895, **71**, 283.

gomeryshire it occurs in the Lower Silurian; and the chief deposits in the United States likewise occur in this same formation. Again, at Sala in Sweden, it is found in granular limestone, and in Freiberg in a schistose gneiss, older than the carboniferous system. Sulphide of lead also occurs in combination with the sulphides of antimony and copper in the minerals zinckenite, $PbSb_2S_4$, and bournonite, $CuPbSbS_3$. In addition to these ores, lead carbonate occurs as the mineral cerussite, $PbCO_3$, found in some localities, as in the neighbourhood of Aix-la-Chapelle, and of Santander in Spain, in sufficient quantity to be worked. It is also found in the lead mines of Cornwall and Devonshire, in Yorkshire, at Leadhills in Scotland, and at Seven Churches in County Wicklow. Other naturally occurring compounds of lead are the basic chloride occurring as the minerals matlockite, Pb_2Cl_2O, and mendipite, $Pb_3Cl_2O_2$; and sulphate of lead or anglesite, $PbSO_4$, found associated with galena and carbonate of lead at Leadhills and in other localities. Again we have a basic sulphate called lanarkite, $PbO+PbSO_4$; leadhillite, $PbSO_4+3PbCO_3$; phosgenite, $PbCl_2+PbCO_3$; stolzite or lead tungstate, $PbWO_4$; wulfenite or lead molybdate, $PbMoO_4$; crocoisite or lead chromate, $PbCrO_4$; pyromorphite or lead phosphato-chloride, $3Pb_3P_2O_8+PbCl_2$; mimetesite or lead chloro-arsenate, $3Pb_3As_2O_8+PbCl_2$; as well as compounds of lead with the rarer elements such as selenium, tellurium, selenic acid, vanadic acid, &c.

By far the greater quantity of the total lead brought into the markets of the world is derived from galena. The total production from all sources in 1895 was 616,794 tons, the amounts from the various countries being as follows:—

	Tons.		Tons.
Spain	152,620	Belgium	13,500
United States	145,906	France	8,758
Germany	100,753	Austria	7,570
Mexico	57,000	Canada	2,628
New South Wales	50,000	Hungary	2,113
Great Britain	40,196	Japan	950
Italy	19,605	Russia	910
Greece	13,955	Sweden	330

373 *Smelting of Lead.*—Lead is an easily reducible metal requiring but simple processes for its production, and was produced in England during the Roman occupation in a variety

of localities. Numerous pigs of Roman lead have been found bearing Latin inscriptions. Whether lead was reduced in England before this period appears doubtful; the remains of rude furnaces in which lead ore was smelted in early times are, however, found in Derbyshire and elsewhere, and are termed *boles* by the inhabitants. In these furnaces the heat was not urged by an artificial blast of air, but piles of stone were built on the western brow of some eminence so as thus to employ the natural currents of air on mountainous places. A mixture of ore and charcoal was introduced into the interior of these furnaces, and after the operation the lead ran out at the bottom.

The form of furnace next employed was the *ore-hearth*, a small rectangular blast-furnace blown by bellows worked by means of a water-wheel.[1] This furnace is still in use and will be hereafter described. Other and larger blast-furnaces are in use in various lead-smelting districts.

About the middle of the eighteenth century lead-smelting in reverberatory furnaces appears to have been introduced into England from Flintshire, where it was in use in the year 1698.

Three distinct processes are employed for lead-smelting. The first of these, known as the *air reduction process* (Percy), is employed when the ore consists mainly of galena, and is free from silica and the sulphides of other metals. The second, or *carbon reduction process*, is employed for less pure ores, and consists in the roasting of the ore and the subsequent reduction of the lead oxide by carbonaceous matter. The third process is known as the *precipitation process*, the reduction of the lead being effected by metallic iron, and this is chiefly practised in France and Germany, where the ore contains other metals, such as copper, antimony, and arsenic.

It is, however, to be remembered that two or even three of the above processes are often worked in the same furnace with the same charge of ore.

In the *air reduction process* the galena is roasted in a reverberatory furnace until a portion of the sulphide is converted into oxide and sulphate; the temperature is then raised when metallic lead is formed together with sulphur dioxide. The following reactions are usually given as representing the inter-

[1] See H. L. Pattinson, "Description of Lead-Smelting in the North of England." *Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-on-Tyne*, vol. 2, part i.

action of the unaltered lead sulphide with the oxide and sulphate :—

$$2PbO + PbS = 3Pb + SO_2$$
$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

In presence of an excess of sulphur dioxide, however, lead is partially reconverted into sulphide and sulphate :—[1]

$$2Pb + 2SO_2 = PbS + PbSO_4.$$

The reverberatory furnaces used for the English process of lead-smelting are of two kinds, the Flintshire furnace and the flowing furnace. The difference between these is that in the first the slag is raked out in pasty lumps, whereas in the flowing furnace the slag is tapped out in the molten state and termed run-slag. The reaction which takes place in reduction is identical in both cases.

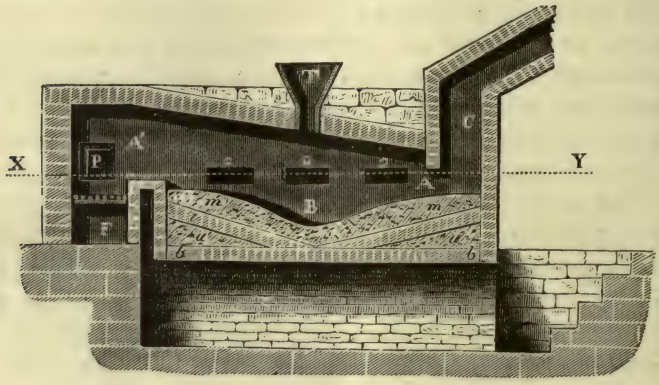


Fig. 157.

Fig. 157 shows the construction of the Flintshire furnace. The usual charge of ore is 20 cwt. This is introduced by means of a hopper (T) in the arch of the furnace. The hearth of the furnace (B) is hollowed out as shown in the figure to permit the lead to flow through a tapping hole, into an iron pot placed in front of the furnace. The charge is evenly spread over the surface and gently heated, the ore being well rabbled at intervals, and the temperature carefully regulated by opening or closing the various doors, so as to maintain the mass as hot as is possible without causing it to clot together; a por-

[1] Jenkins and Smith, *Proc. Chem. Soc.* 1897, 104.

tion of the sulphide is oxidised to oxide and sulphate, and the mass thus prepared for the following stage of the operation. During this part of the process the skimmings from the lead run off from the previous operation, which consist chiefly of lead containing a little sulphide, are added, and are quickly acted on by the lead oxide and sulphate with formation of lead, which is run off from the tap-hole and contains more silver than the subsequent portions of the metal. After about two hours the temperature is raised to a bright red-heat, lead being formed in quantity, whilst from time to time, in addition to stirring the mass, a small quantity of lime is added to stiffen the unreduced portion. This part of the process extends over an hour, and then for three-quarters of an hour the temperature is further raised and an additional small quantity of lime added, which besides lessening the fusibility of the mass also liberates any lead oxide, which may have combined with the silica, and allows it to be reduced by the lead sulphide. Finally the furnace is raised for three-quarters of an hour to the highest attainable temperature and a sufficient quantity of lime added to partially solidify the slag, which is raked out, and the lead run off from the tap-hole in the usual manner. The *grey slag* obtained may contain as much as 40 per cent. of lead, and is further worked up in the slag-hearth (p. 698).

A similar method is adopted at Bleiberg in Carinthia for working the calcareous galena, a different form of furnace being, however, employed. This furnace is very much smaller than either of the English lead furnaces and only 300 lbs. of ore are worked at once, the object being to conduct the process with accuracy and precision, the small quantity worked upon placing the calcination better under command. As soon as the charge is placed on the floor of the furnace it is heated to dull redness, and the roasting is completed in from three to four hours. This constitutes the first stage of the process, in which the sulphide is partially converted into oxide and sulphate of lead. As in the English process, the temperature is now raised and the double decomposition between the oxidised products and the undecomposed sulphide, which has already been described, takes place. The reduction of the lead appears to go on in this process at a lower temperature than in the working of the English process, and the virgin lead (*Jungfernblei*) thus obtained is believed to be purer than the lead obtained in the Flintshire furnace. This is especially the case in Bleiberg, as well as in certain Belgian works, where con-

siderable quantities of impurities are contained in the lead ore. These remain behind in the slag whilst the lead is run off in the pure state.

In Scotland and the north of England, where a very pure ore is worked, lead-smelting is conducted in shallow hearths or Scotch furnaces shown in Fig. 158. The hearth (A) is first filled with peat which is then ignited, and ore added from time to time in quantities of about a dozen pounds weight, the temperature being kept up by a blast of air sent in at the back of the furnace. The reduced lead sinks down to the bottom and flows out along the channel in the *work-stone* (C) into the heated pot (D). A considerable amount of lead is volatilised as fume

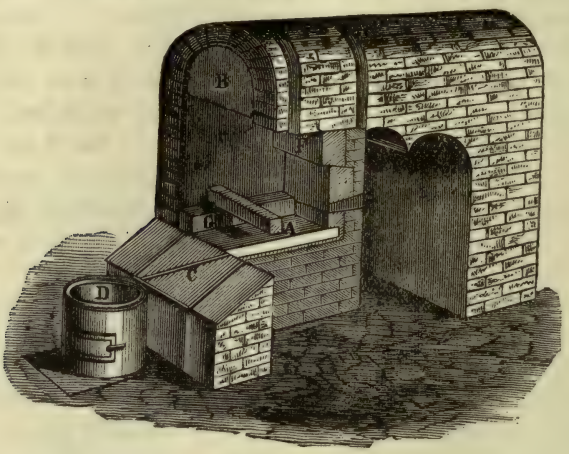


FIG. 158.

in this process: this passes through the flue (B) to long collecting chambers in which it is deposited. The lead thus obtained is said to be purer than that prepared in the Flintshire furnace, but the cost of smelting in this ore-hearth is greater than when the Welsh method is used.

For the reduction of impure ores or for the working up of slags from the other processes a *slag-hearth* or a small blast-furnace (Fig. 159) is used, of about 0·5 metre in height, containing a square space (C), the sides of which are built of iron plates. The blast of air enters by the tuyere (T), and the reduced metal runs through a hole in the plate into the vessel (M). The hearth is filled with fuel and the ore thrown on to the top of the fuel. The ore is at first converted into a mixture of sulphide, sulphate and oxide, and these undergo mutual decom-

position with evolution of sulphur dioxide as they descend to the lower portion of the hearth, where the temperature is higher.

Reduction of Lead in Blast-Furnaces.—The method of alternate oxidation and reduction is certainly the simplest method of lead-smelting, but is only applicable in the case of galena which does not contain any quantity of the sulphides of other metals, with the exception of silver. For ores such as those which occur in the Harz, where the galena is mixed with iron and copper pyrites, zinc blende, fahl-ore, bournonite, and zinckenite, the blast-furnace method gives the best results, and this method is also suitable for the reduction of the oxides or carbonates of lead. Of late years the construction of the blast-furnace for this purpose has been much improved, and the method is very largely used, especially in Germany and America, and to some extent in this country.

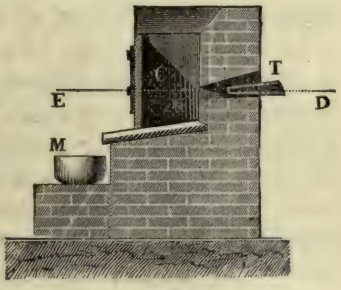


FIG. 159.

The type of furnace most used in Germany is that known as the Piltz furnace, which is circular in section, and about 25 feet in height, and tapers from 7 feet diameter at the top to about 5 feet at the bottom. It is usually built of brick, except at the tuyere zone, which is constructed of iron, and is water jacketed. The Rachette furnace largely employed in America is very similar in principle, but has a rectangular section.

Where the ores to be reduced consist chiefly of oxides, the only reducing agent necessary is carbon; but if any considerable quantity of sulphur is present, iron must be added. Instead of metallic iron it is now usual to add a rich iron slag, which is itself converted into iron in the blast-furnace, and combines with the sulphur to form iron sulphide. If the ores contain more than 12–15 per cent. of sulphur they are usually subjected to a preliminary process of roasting.

A somewhat similar treatment of washed lead ores by metallic iron in blast-furnaces is adopted at Pongibaut, in Puy-de-Dôme and of siliceous ores at Couëron.

Softening of Lead.—The lead produced in these processes is hard, owing to the presence of small quantities of silver, antimony, copper, and iron. The former is removed by a special process, which is described later, and which enables the valuable

silver to be recovered. For the purpose of removing the other impurities, the lead is melted in a reverberatory furnace at a low temperature; a considerable quantity of the less fusible metals at once separates out on the surface as a dross and is quickly removed, and the remainder is oxidised together with a portion of the lead by allowing air to pass over the surface, an oxide dross separating out, which is removed as it is formed. In some cases the process is now carried out by forcing a stream of air through the molten metal in a large iron pot, but this is a very slow operation, as the temperature must be kept low in order to avoid oxidising the lead itself to any large extent.

374 *Desilverisation.*—Ordinary lead obtained by any of the above-mentioned processes always contains silver, and a very considerable proportion of the silver which now comes into the market is obtained from argentiferous galena. In former times the only process by which this silver could be extracted was by cupellation, by which the whole of the lead is oxidised, whilst metallic silver remains behind. The oxide has then to be again reduced in a reverberatory furnace to metallic lead. It is, however, generally admitted that the process of cupellation cannot be economically carried on in the case of lead which contains less than 8 oz. of silver to the ton, and consequently, as very large quantities of lead are brought into the market containing smaller percentages than this, the whole of this amount of silver was lost until Hugh Lee Pattinson, in the year 1833 obtained a patent for an improved method of separating silver from lead, which soon came into general use and by which large quantities of silver are now extracted from lead.

This method depends upon the fact that if lead containing a small quantity of silver be melted, and the melted mass allowed to cool, a point is reached at which pure lead begins to crystallise out. If the crystals of lead which are thus formed be then withdrawn from the remainder of the metal, and this process continued until the greater part of the lead has been separated, it is found that the liquid which remains contains most of the silver. In order to render this process economical the lead requires to be repeatedly crystallised in a series of iron pots, the lead rich in silver gradually accumulating towards one end of the series, whilst the desilverised or market lead is obtained at the other end.

The melted lead is first thoroughly skimmed, then the fire is

withdrawn and the lead allowed to cool, care being taken to break off and mix with the liquid mass any portion that may solidify on the sides of the pot. When the temperature reaches a certain point, small crystals of lead begin to form, and at this point the whole mass of metal is continually stirred with an iron rod, whereby the crystals sink to the bottom of the pot and accumulate in considerable quantity. A perforated ladle is now introduced by means of which the crystals are removed. The operation is thus carried on in successive stages until two-thirds or even three-fourths of the original lead is removed from the pot. By this means in an actual working 846 cwt. of original lead was separated into 36 cwt. of rich lead containing 160 to 170 ounces of silver per ton, and 810 cwt. of poor lead containing 7 to 10 dwt. of silver per ton. The silver is then extracted from the rich lead by the process of cupellation. (For a description of this process see Silver, p. 345.)

A modification of the Pattinson process, known as the Luce-Rozan process, is now frequently adopted in place of the original method. For this only two pots are necessary, viz., an upper or melting pot, and a lower or crystallising pot. The former holds about 7 and the latter about 21 tons.

The mode of working the plant is as follows[1]: The crystallising pot may be supposed to contain 14 tons of lead crystals from a previous operation, and the melting pot 7 tons of lead of similar silver content, already melted; a moderate fire is set away in the fire-grate of the crystallising pot, and the contents of the melting pot skimmed of their dross; the hot lead from the latter is then run on to the warm crystals in the crystallising pot, and with the aid of the moderate fire already referred to, the whole contents of this pot (now 21 tons) are rapidly brought into a melted and working condition, when the charge is carefully skimmed; the melting pot is at the same time charged with 7 tons of lead, from a previous operation containing one-half the amount of silver in the lead then being worked up, as this will be the assay of the crystals resulting from the operation about to be performed in the crystallising pot. The fire under the latter is then drawn, and steam at fifty to fifty-five pounds pressure per square inch admitted and distributed evenly by means of a baffle plate. To hasten the cooling and consequent crystallisation, thin streams of water are allowed to run on to the surface of

[1] Cookson, *Trans. Newcastle Chem. Soc.* 1878.

the lead, the crystallisation being more perfect than in the old Pattinson process. As soon as two-thirds of the lead has crystallised out, the rich liquid lead is tapped off, the crystals being retained in the pot by means of perforated plates. The liquid lead is run into moulds and awaits its turn for further treatment. The proportion of silver in the crystals is thus reduced to one half, whilst that in the liquid run off is doubled, and this process of recrystallising is repeated as in Pattinson's process, until the crystals are sufficiently poor in silver not to require further treatment, and the rich lead is worked up until its silver contents are of the standard fit for the refinery.

This process has the advantage over that of Pattinson that a great saving is effected in fuel and the cost of labour, and also that, except in the case of very hard lead, no further softening process is necessary. The original outlay and expenses for repairs are, however, considerably greater.

Another process for desilverising lead is known as Parkes's or Karsten's zinc process. It has already been mentioned in the chapter on alloys that molten lead and zinc do not mix in all proportions, lead being capable of taking only 1·6 per cent. of zinc whilst zinc takes up only 1·2 per cent. of lead. Karsten, in 1842, concluded from experiments which he made on the subject that lead gives up all the silver which it contains if melted with zinc, but he did not apply this conclusion to practical metallurgy. In the year 1850, Alexander Parkes, of Birmingham, patented a process for extracting silver from lead by the above-mentioned reaction. For a ton of lead containing 14 oz. of silver, 22·4 lbs. of zinc is needed; if containing 21 oz., 33·6 lbs. of zinc is added, and if containing 28 oz. of silver 44·8 lbs. of zinc is required. The alloy of zinc and silver rises to the surface during cooling, and when it solidifies it is withdrawn by means of a perforated ladle. In order to remove the small quantity of zinc which is dissolved in the pure lead, the mixture is heated to dull redness in a current of air, the zinc thereby being oxidised, whilst the main portion of the lead remains behind in the marketable state. Silver is separated from the alloy of zinc in the manner already described under Silver (p. 351).

Gold and copper, which sometimes occur in market lead, can be separated from it in the same way, inasmuch as these metals alloy with zinc even more readily than silver does, and this process has been satisfactorily carried out in England by Baker.

A similar method is employed in the Harz; the lead is there melted with 0·16 per cent. of zinc, and the alloy is obtained as a scum on the surface, having the composition :—

Lead	89·46
Zinc	5·78
Copper	4·52
Silver	0·243
	100·003

On a second addition an alloy having the following composition is obtained :—

Lead	91·05
Zinc	5·21
Copper	3·50
Silver	0·238
	99·998[1]

Market lead almost always contains traces of antimony, copper and iron, and occasionally of zinc, nickel and bismuth, whilst the silver which it contains varies from one part in 40,000 to one part in 200,000, but since the introduction of the method of desilverising by zinc, and purification by steam the purity of the commercial lead has very much increased. An analysis by Hampe of a refined lead from the Harz, gave the following results :—

Antimony	0·0057 per cent.
Copper	0·0014 „
Iron	0·0023 „
Zinc	0·0008 „
Nickel	0·0007 „
Bismuth	0·0055 „

showing a total impurity of only 0·0164 per cent.

375 *Chemically pure lead* is prepared according to Stas[2] as follows :—A solution of acetate of lead is heated in a leaden vessel in contact with thin sheet lead to a temperature of from 40° to 50° in order to precipitate silver and copper. The filtrate is then poured into pure, very dilute sulphuric acid, and the lead sulphate which is formed, carefully washed with a solution

[1] Rammelsberg, *Ber. Entw. Chem. Ind.* 935.

[2] *Bull. Acad. Roy. Belg.* **10**, 294.

of ammonium carbonate and ammonia, lead carbonate being in this way formed. A portion of this is then converted into lead oxide by carefully heating in a platinum basin, whilst to the remaining portion pure dilute nitric acid is added in such quantity that a portion of the carbonate remains undissolved. The oxide of lead is then added to the boiling solution of the nitrate in order to precipitate traces of iron, and the filtered solution poured into one of pure ammonium carbonate. The precipitated lead carbonate is then reduced by means of potassium cyanide, and the metal thus formed fused a second time with the cyanide, when it assumes in the molten state a convex surface like mercury.

Lead can easily be crystallized in the form of regular octohedra by melting, allowing the molten metal to partially solidify, and pouring off the portion which is still liquid. Similar crystals are obtained by the electrolytic decomposition of solutions of lead salts, using a strong current, but with weak currents plates belonging probably to the monosymmetric system are formed. Similar crystals to these separate out in bright shining arborescent forms, known as the lead tree, if a piece of zinc be hung up in a solution of sugar of lead. Lead has a specific gravity of 11·254, or after it has been poured into water of 11·363. On hammering it cracks and becomes lighter, but if it be pressed it attains a specific gravity of 11·388. It is soft and tough. It may be cut with a knife, and leaves a streak upon paper. It can easily be rolled out to thin foil, but it cannot be drawn out into fine wire. When melted repeatedly it becomes hard and brittle, which is probably due to the formation of a small quantity of oxide. On the large scale this oxide may be removed by poling or stirring the molten mass up with a pole of green wood. The presence of antimony, zinc, bismuth, arsenic, and silver increases the brittleness of lead. Lead belongs to the class of white metals, though it has a decidedly bluish-grey tint indicated by the expression lead-grey. A freshly cut surface possesses a bright lustre, which, however, soon becomes dull from superficial oxidation. By the electrolysis of lead nitrate, Wöhler obtained a deposit on the negative pole of crystallised leaflets of lead possessing a red colour like that of copper. These did not dissolve in dilute acids whilst they were soluble in hot nitric acid, and on dissolving, the colour resembled that of copper to the last moment.[1] Lead melts at

[1] *Ann. Chem. Pharm.* Suppl. 1863, **2**, 135.

326°, and begins to volatilise at a bright red-heat, boiling rapidly before the oxyhydrogen blowpipe. It cannot, however, be distilled in closed vessels like zinc, although when zinc is extracted from ores containing lead, the vapour of zinc is mixed with vapour of lead, and a considerable portion of the loss experienced in the ordinary processes of lead-smelting is due to this cause.

Metallic lead is largely employed in the arts for a great variety of purposes on account of its softness and pliability, its low melting point, the difficulty with which it undergoes oxidation, and the fact that it withstands the action of water and of many acids better than most of the common metals.

COMPOUNDS OF LEAD.

Lead and Oxygen.

376 Lead forms five compounds with oxygen :—

Lead suboxide, Pb_2O,
Lead monoxide, PbO,
Lead sesquioxide, Pb_2O_3,
Red-lead, Pb_3O_4,
Lead dioxide, PbO_2.

The most important of these is the strongly basic monoxide, which corresponds to the chief series of salts, in which lead is divalent. The dioxide acts as a weak basic oxide towards strong acids, as an acidic oxide to strong bases, and also behaves in many respects as a peroxide. The trioxide and red-lead are probably salts formed by the combination of the basic monoxide and the acidic dioxide (p. 710).

Lead Monoxide, PbO.—This compound was known to the ancients, as it is formed when lead is heated in contact with the air, and is, therefore, produced in various metallurgical processes. The different forms of this compound were, however, regarded as different substances, giving rise to the names *plumbum ustum*, *scoria plumbi*, *scoria argenti*, *galena*, *μολύβδαινα*, *λιθάργυρος*, &c. When lead is heated to its point of volatilisation in the air, it takes fire and burns with a white light, yielding this oxide which formerly received the name of flowers of lead or *flores plumbi*. Lead, when heated in the air, becomes covered with

a grey film, and if the surface be continually renewed, becomes wholly converted into lead-ash, a yellowish-grey pulverulent mixture of metallic lead and yellow monoxide, which, if heated in the air for a longer time, is wholly converted into the latter. This yellow oxide is termed *massicot*, whilst the other form of lead monoxide termed *litharge*, is obtained at a temperature at which the oxide fuses, solidifying to a scaly shining mass sometimes of a yellow tint, sometimes rather inclined to red.

Crystallised oxide of lead also occurs in nature as a mineral found near Vera Cruz (Nöggerath). The crystals may also be artificially obtained by allowing litharge to cool slowly; it forms rhombic octohedra which are sometimes also found as a deposit in the lead furnaces (Mitscherlich), and red quadratic crystals may also be obtained (Geuther). Lead oxide possesses a colour varying from lemon-yellow to reddish-yellow, and on heating assumes a brownish-red tint. Its specific gravity at 4° is 9·36 (Joule and Playfair). It is reduced to the metallic state by carbonic oxide at 100°, and by hydrogen at 310°. Litharge is largely used in the arts, especially for the manufacture of flint-glass, and as a glaze for earthenware; it is also used for the preparation of red-lead, lead acetate, lead nitrate, white-lead, lead-plaster, and drying oils. Commercial litharge contains carbon dioxide and water absorbed from the air, which may be removed by ignition. Not infrequently it contains small quantities of iron oxide and copper oxide, the latter easily removable by ammonia.

Basic Lead Hydroxide, $Pb_2O(OH)_2$.—This substance is obtained as a white precipitate by the action of air and water free from carbonic acid upon the metal, or is thrown down as a white precipitate on the addition of ammonia or a fixed alkali to a lead salt. It is obtained in colourless quadratic crystals by exposing a cold solution of lead monoxide in caustic potash to the air, the carbon dioxide in the latter converting the caustic potash into potassium carbonate.

The compound $Pb_3O_2(OH)_2$ is formed according to Payen as follows:—100 parts of a solution saturated at 16° of basic acetate of lead, $Pb_3O_2(C_2H_3O_2)_2$, are added to 50 volumes of cold water which has previously been well boiled: a mixture of 20 parts of ammonia and 30 parts of boiled water is then added and the solution allowed to stand at a temperature of 25–30° when the above hydrate separates out in glittering octohedra.

At 130° lead hydroxide loses a portion, and at 145° the whole of its water, being then converted into lead oxide. The hydroxides of lead as well as the oxide turn moistened red litmus paper blue as they are somewhat soluble in water. They act as strong bases but also combine with certain basic oxides. Thus when lead oxide is fused with the alkalis, alkaline earths, and other metallic oxides, a glass is formed and in consequence of this lead oxide attacks clay crucibles. It dissolves also in caustic potash and soda as well as in lime and baryta water yielding yellow liquids. The lime compound is slightly soluble in water and crystallises on cooling in white needles (Berthollet, Karsten).

Lead Suboxide, Pb_2O, is formed when lead oxalate is heated in an atmosphere free from oxygen to a temperature below 300° (Dulong):—

$$2PbC_2O_4 = Pb_2O + CO + 3CO_2.$$

It is a black, velvety powder, which when heated in absence of air is decomposed into metal and the monoxide. When lead is melted in the air the surface becomes covered first with a grey film, which, according to Berzelius, consists of the suboxide. The suboxide has by some been considered to be an intimate mixture of finely-divided lead and the monoxide. Against this view, however, is to be placed the fact that mercury does not dissolve metallic lead from this grey powder, whilst a solution of sugar which readily dissolves lead monoxide, does not take up any from this substance. After heating, dilute acetic acid or a solution of sugar does dissolve out lead oxide, whilst metallic lead remains behind in the coherent state.

Lead Sesquioxide, Pb_2O_3, is formed when a solution of sodium hypochlorite is carefully added to a cold caustic potash solution of lead oxide (Winkelblech), or when a solution of red-lead in acetic acid is precipitated by very dilute ammonia. It is a reddish-yellow amorphous powder which does not part with the whole of its water at 150°. It is decomposed by acids into the monoxide and dioxide, and is, therefore, considered to be a compound of these two, PbO, PbO_2, and may be termed *lead metaplumbate* (p. 710).

Red-Lead or Minium, Pb_3O_4.—This compound was described by Pliny, under the name of *minium*, but it was at that time not sufficiently distinguished from cinnabar and the red sulphide of arsenic. Dioscorides, however, mentions that it can be pre-

pared from white-lead : "*cerussa, si coquatur rufescit ;*" and Geber says : "*plumbum aduritur et fit minium.*"

Red-lead is usually prepared by carefully heating very finely-divided pure massicot or white-lead. For this purpose the oxide is heated for about twenty-four hours either on the flat hearth of a reverberatory furnace, or in barrel-shaped vessels open at both ends, the mass being frequently stirred and the heat not allowed to rise above dull redness. The brightness and beauty of the colour much depends on the care spent on the roasting, as these properties are not wholly influenced by the absorption of oxygen, but more especially by the particular molecular condition of the material and this is produced only at a given temperature.

Red-lead is a scarlet crystalline granular powder, which, on heating, first assumes a finer red colour and afterwards turns violet and lastly black, but on cooling regains its original tint. On ignition it loses oxygen and is converted into the monoxide. Its specific gravity varies from 8·6 to 9·1. Commercial red-lead frequently contains the yellow oxide litharge mixed with it, which may be extracted by repeatedly digesting it with a solution of lead acetate. Red-lead is largely used as a paint and also in the preparation of flint-glass. For both of these purposes it is necessary that it should be as free as possible from iron, and in this case it is not infrequently prepared from white-lead. Red-lead is also adulterated with oxide of iron, red bole, powdered heavy spar, and brick-dust. These substances remain undissolved when red-lead is digested in warm dilute nitric acid to which a little sugar has been added, whilst the red-lead is completely dissolved. Boiling hydrochloric acid extracts sesquioxide of iron from the impure oxide with formation of lead chloride and liberation of chlorine. Like the trioxide it is decomposed by acids into the monoxide or a corresponding salt, and the dioxide, and is therefore regarded as a compound of two molecules of the former and one of the latter, $2PbO, PbO_2$, and may be termed *lead orthoplumbate* (p. 710).

377 *Lead Dioxide, Lead Peroxide* or *Puce-coloured Oxide of Lead,* PbO_2.—This substance was discovered by Scheele, who observed that red-lead is coloured brown when treated with chlorine water, whilst Priestley found that nitric acid produces the same reaction. The properties of the puce-coloured lead oxide were more exactly examined by Proust and Vauquelin.

Lead dioxide may be prepared according to a variety of

methods. The simplest plan is by acting upon red-lead with dilute nitric acid :—

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

It is likewise obtained by the action of chlorine upon lead salts in the presence of alkalis (Wöhler), or by treating a hot solution of a pure lead salt with a soluble hypochlorite (Böttger) :—

$$PbO + NaClO = PbO_2 + NaCl.$$

It is obtained in the dry way by fusing 4 parts of lead monoxide 1 part of potassium chlorate, and 8 parts of nitre (Liebig and Wöhler). Lead oxide is also converted into the peroxide by the action of ozone as well as of hydrogen peroxide, and it is deposited in crystalline scales at the positive pole when a lead salt is decomposed by means of a galvanic current.

This substance is found native in the form of plattnerite, which crystallises in black hexagonal prisms having a specific gravity of 9·4. The artificial peroxide sometimes occurs in the form of brownish-black six-sided tablets, but is generally a dark brown powder having a specific gravity of 8·9 to 9·2.

Lead dioxide decomposes on heating into oxygen and the monoxide. It loses oxygen when simply exposed to sunlight, red-lead being formed. It has a strongly oxidising action and when triturated with one-sixth of its weight of sulphur, it takes fire and burns with a brilliant flame, forming sulphide of lead.[1] Aqueous hypophosphorous acid is at once oxidised with formation of lead phosphate. When immersed in sulphurous acid gas at ordinary temperatures it becomes red-hot and is converted into lead sulphate, whilst nitrogen peroxide and even ammonia converts it into lead nitrate. A large number of organic acids and other carbon compounds when triturated with it likewise cause evolution of light and heat. When treated with aqueous hydrochloric acid, chloride of lead and free chlorine are formed. Lead dioxide is often employed as an oxidising agent, as for instance, in the analysis of organic substances containing sulphur in order to separate the sulphur dioxide from carbon dioxide. The mixture of lead nitrate and dioxide obtained by treating red-lead with nitric acid, is employed under the name of oxidised red-lead in the manufacture of lucifer matches.

Lead dioxide is capable of acting as a weak basic oxide, yielding the unstable tetravalent lead salts, and also as a

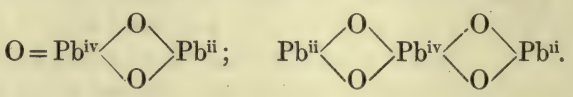
[1] Vauquelin, *Ann. Chim. Phys.* **62**, 221.

peroxide and an acid-forming oxide, forming compounds to which the name *plumbates* has been given. *Orthoplumbates* having the composition M'_4PbO_4 and *metaplumbates* M'_2PbO_3 are known, and the free *metaplumbic acid*, $PbO(OH)_2$ or H_2PbO_3, is deposited at the positive pole as a black lustrous substance on the electrolysis of a slightly alkaline solution of lead sodium tartrate.

Potassium Metaplumbate, $K_2PbO_3 + 2H_2O$, is obtained in crystals by fusing lead dioxide with excess of caustic potash in a silver crucible, dissolving in water and evaporating in a vacuum.[1] The solution gives with most metallic salts precipitates of the corresponding metaplumbates.

The orthoplumbates of the alkaline earths are obtained by heating the carbonates or hydroxides with lead monoxide in presence of air, the *calcium* salt, Ca_2PbO_4, crystallising with 4 molecules of water in almost colourless microscopic transparent crystals. These compounds evolve oxygen on strongly heating, and it has been proposed to utilise this method for obtaining oxygen from the atmosphere on the large scale, and this salt has also been used as an oxidising agent.[2]

As already mentioned lead sesquioxide and red-lead may be regarded as the metaplumbate and orthoplumbate of lead, their constitution being represented by the formulæ:—



Lead and the Halogens.

378 *Lead Fluoride*, PbF_2.—This compound is obtained by heating lead oxide or carbonate with hydrofluoric acid, or by precipitating a lead salt with a soluble fluoride. It is a white powder and is almost insoluble in water and in hydrofluoric acid, but readily soluble in hydrochloric and nitric acids. When treated with ammonia an easily soluble basic fluoride is formed. If a solution of chloride of lead be precipitated with sodium fluoride the compound PbClF is formed. This chloro-fluoride of lead is slightly soluble in water, dissolving without decomposition (Berzelius).

Lead Tetrafluoride, PbF_4.—This compound is probably formed by the action of strong sulphuric acid on the acid plumbo-

[1] *Ann. Chim. Phys.* 1844 [3], **12**, 490.

[2] Kassner, *Arch. Pharm.* 1890, **228**, 109; 1894, **232**, 375; 1895, **233**, 501.

fluoride, $3KF,HF,PbF_4$, but has not been obtained in the pure state. The above double salt, which is isomorphous with the analogous tin derivative, is obtained by the action of hydrofluoric acid and potassium fluoride on lead tetracetate, or by fusing lead dioxide with potassium fluoride and treating the product with hydrofluoric acid. It forms monosymmetric needles which evolve hydrofluoric acid at 230°, and at a higher temperature yield free fluorine.[1]

Lead Chloride, $PbCl_2$.—Dioscorides mentions that yellow oxide of lead when brought in contact with common salt and warm water becomes white. After the discovery of silver chloride, to which the name of horn-silver was given, the corresponding lead compound was termed horn-lead (*plumbum corneum*). Lead chloride occurs native in the craters of volcanoes as the mineral cotunnite. Lead combines with chlorine, but slowly, and without incandescence. Dilute hydrochloric acid dissolves the metal only in the presence of the air, and then but slowly. The boiling concentrated acid, however, converts it into chloride with evolution of hydrogen gas. Lead chloride is easily prepared by the action of hydrochloric acid on the oxide or carbonate, and also by the precipitation of a tolerably concentrated solution of a lead salt by means of hydrochloric acid or a soluble chloride. It is thus obtained in the form of a white crystalline precipitate, which dissolves in 135 parts of water at 12·5° and in less than 30 parts at 100°, crystallising on cooling in white silky rhombic needles, having a specific gravity of 5·8. It is less soluble in dilute hydrochloric acid and solutions of chlorides than in pure water, but dissolves more freely in concentrated hydrochloric acid; hence a precipitate may be obtained by adding water to the latter solution, whilst the aqueous solution is precipitated by hydrochloric acid. It also dissolves readily in the solutions of the acetates and thiosulphates of the alkali metals. When heated in absence of air lead chloride melts at about 485°, solidifying on cooling to a white translucent horny mass; it volatilises at a temperature of 861–934°, the vapour having a density of 5·8, corresponding to the formula $PbCl_2$.[2]

Lead yields a large number of oxychlorides. The compound $PbCl_2,PbO$ occurs as the mineral matlockite and may be obtained artificially by igniting the chloride in the air till no further

[1] Brauner, *Journ. Chem. Soc.* 1894, i. 393.

[2] Roscoe, *Proc. Roy. Soc.* 1878, **27**, 428.

fumes are evolved. The mineral mendipite has the composition $PbCl_2,2PbO$, and numerous others, some of which contain water of crystallisation have been prepared. The hydrate $PbCl_2,PbO + H_2O$ which may also be formulated as lead hydroxychloride Pb(OH)Cl, was formerly prepared by a process patented by Pattinson in 1849. In this process chloride of lead is first prepared from finely pulverised galena and concentrated hydrochloric acid; this is then dissolved in water and mixed with lime-water in certain definite proportions; a snow-white precipitate having the composition above, is thrown down, which was at one time used as a paint in place of white-lead. A hydrated oxychloride is likewise obtained by warming lead oxide with a solution of common salt (Scheele), caustic soda being at the same time produced. In the year 1787, Turner took out a patent for the purpose of preparing caustic soda by this reaction, and found that the residue when heated became anhydrous and possessed a yellow colour. This oxychloride is known under the name of *Turner's yellow* or *patent yellow*. Vauquelin then showed that when lead chloride and lead oxide are fused together a yellow-coloured body is obtained. This is now known as *Cassel yellow*, and is usually prepared by fusing together 1 part of sal-ammoniac and about 10 parts of massicot, minium, or white-lead; a part of the sal-ammoniac sublimes undecomposed, and the resulting compound contains about 1 molecule of chloride to 7 molecules of oxide; part of the lead being at the same time reduced by the ammonia.

Lead chloride also yields a number of double salts with the chlorides of other metals.

Lead Tetrachloride, $PbCl_4$.—A solution of this compound is formed by dissolving the dioxide in well-cooled hydrochloric acid, but it is best prepared by passing chlorine into lead dichloride suspended in hydrochloric acid. On addition of ammonium chloride *ammonium plumbichloride*, $(NH_4)_2PbCl_6$, crystallises out, which on addition to well-cooled sulphuric acid yields the tetrachloride as a yellow refractive fuming liquid, which readily decomposes into the dichloride and chlorine. It has a specific gravity of 3·18 at 0°, solidifies at −15° to a yellowish crystalline mass, and yields a hydrate with a small quantity of water, but in presence of an excess of the latter is decomposed into lead dioxide and hydrochloric acid.[1]

[1] Friedrich, *Monatsh.* 1893, **14**, 505; Classen, *Zeit. Anorg. Chem.* 1893, **4**, 100.

Lead Bromide, $PbBr_2$.—This compound closely resembles the chloride. It is obtained by treating lead oxide with aqueous hydrobromic acid, or by precipitating a lead salt with a solution of potassium bromide, when it is thrown down in the form of white shining needles. It dissolves in hot water and has a specific gravity of 6·6. On heating in a closed vessel it fuses forming a red liquid which on cooling solidifies to a white horny mass. Fused in contact with the air it emits white fumes and leaves a residue of oxybromide, $PbBr_2,PbO$, forming a pearly yellow mass.

Lead Iodide, PbI_2.—Hydriodic acid easily dissolves lead, and the iodide separates out from a concentrated solution in beautiful yellow crystals (Deville). When a solution of a lead salt is mixed with a soluble iodide a yellow precipitate of lead iodide is formed. This is soluble in 1235 parts of cold, and 194 parts of boiling water, giving rise to a colourless solution from which the iodide separates out on cooling in yellow laminæ resembling those of mosaic gold. The specific gravity of this compound is 6·1; on heating it becomes reddish-yellow, then of a bright red colour, and lastly assumes a brownish-black colour; it melts in a closed tube to a reddish-brown liquid which solidifies to a yellow crystalline mass. Like the chloride and bromide it easily forms basic salts.

Lead and Sulphur.

379 *Lead Sulphide*, PbS, occurs in nature as galena, crystallised in cubes or in other combinations of the cubic system. It possesses a bluish-grey colour, and has a specific gravity varying from 7·25 to 7·7. This mineral was known to the ancients under its present name, but the fact that it contained sulphur was not recognised until after some time. Thus even Kunkel was unacquainted with this fact, though Boyle[1] was aware that when galena is heated with scrap-iron, metallic lead is formed and recommended this mode of producing lead.

When sulphur vapour is led over metallic lead it takes fire and burns, forming a crystalline sulphide, and even tolerably thick strips of lead take fire in sulphur vapour with vivid glow, depositing half-fused globules of lead sulphide. It can also be prepared by fusing lead oxide with an excess of sulphur. When sulphuretted hydrogen is passed into a solution of lead nitrate,

[1] A hydrostatical way of estimating ores of lead.

an amorphous black precipitate is formed, but if the gas be passed into a dilute solution of the salt containing free nitric acid a crystalline precipitate is obtained, consisting of microscopic cubes (Muck).

Sulphide of lead fuses at a strong red-heat, and when heated in a current of many gases sublimes in cubes which often have a diameter of 1·5 mm. Crystals of galena are often obtained in lead-works in a similar way. On the other hand, octohedral crystals may be obtained by fusing 1 part of the precipitated sulphide with 6 parts of potash and 6 parts of sulphur (Schneider). Nitric acid converts galena, with separation of sulphur, partly into the nitrate and partly into the sulphate, the latter compound being formed in the largest quantity when the acid is strongest. Hot concentrated hydrochloric acid dissolves it with evolution of sulphuretted hydrogen.

When an aqueous solution of a lead salt containing an excess of hydrochloric acid is treated with a small quantity of sulphuretted hydrogen, a yellowish to dark red precipitate is obtained which consists of a double chloride and sulphide of lead. According to Hünenfeld,[1] this precipitate has the composition $3PbS, 2PbCl_2$, whilst Parmentier[2] found the composition $PbS,PbCl_2$; it is converted by an excess of sulphuretted hydrogen into lead sulphide, and loses lead chloride on treatment with hot water.

Lead Sulphate, $PbSO_4$.—This substance is found native as lead vitriol or anglesite in transparent rhombic crystals, isomorphous with those of cœlestine and heavy-spar, or as pseudomorphs of galena. It is obtained as a white powder by precipitating a lead salt with sulphuric acid or a soluble sulphate. If a layer of water be poured on to a saturated solution of potassium sulphate, and a platinum wire on which some lead choride has been fused allowed to dip into the water, crystals of lead sulphate are gradually formed.[3] Lead sulphate has a specific gravity of 6·2 to 6·3. It melts at a red-heat without decomposition. One part of the salt dissolves in 21,739 parts of cold water, and in 36,504 parts of dilute sulphuric acid, whilst concentrated sulphuric acid can take up about 6 per cent. of the compound. It also dissolves in warm ammonia and caustic potash, and in hot hydrochloric acid with formation of lead chloride. Sulphate of lead is likewise very readily

[1] *J. Pr. Chem.* 1836, **7**, 27.
[2] *Compt. Rend.* 1892, **114**, 299.
[3] Manross, *Annalen*, 1852, **82**, 360.

soluble in ammoniacal salts, especially in the acetate; calcium acetate and many other salts also dissolve it.

When lead sulphate is boiled with concentrated sulphuric acid, it is dissolved and is afterwards deposited in crystals, and if the mother-liquor be allowed to stand in contact with moist air crystals of the acid sulphate, $PbSO_4 + H_2SO_4 + H_2O$, similar to those of the corresponding barium salt are formed.

When the normal salt is treated with ammonia, the basic sulphate Pb_2SO_5 or $O<\begin{matrix}Pb\cdot O\\Pb\cdot O\end{matrix}>SO_2$ is formed. The same salt is obtained in microscopic needles when an excess of a hot solution of sodium sulphate is added to basic lead formate (Barford).

Lead and Nitrogen and Phosphorus.

380 *Lead Nitrite* $Pb(NO_2)_2$.—This substance is most readily obtained by decomposing silver nitrite with lead chloride, and concentrating the solution in a vacuum, when yellow prisms separate out, which are easily soluble in water. On evaporating the solution, nitric oxide is evolved, and a basic salt remains behind. If lead nitrate be digested with water in contact with finely-divided metallic lead for a few hours at a temperature of 75°, a yellow solution is formed, which on cooling deposits the basic double salt, $Pb(NO_3)OH + Pb(NO_2)OH$ in glittering yellow plates. Proust, who first obtained this compound, considered it to be a nitrate of a suboxide of lead, whilst Berzelius viewed it as a simple basic nitrite. If its solution be boiled with metallic lead and a large quantity of water, orange-yellow prisms separate out on cooling, having the composition $Pb(NO_2)_2 + Pb(NO_3)_2 + 5PbO + 3H_2O$. This salt was formerly termed *lead hyponitrate*. If lead nitrate be boiled with one and a half times its weight of lead, and fifty times its weight of water for twelve hours in a long-necked flask, pale red needles of basic nitrite of lead, $Pb(NO_2)_2 + 3PbO + H_2O$, are formed. Other basic nitrites of lead are known.

Lead Nitrate, $Pb(NO_3)_2$.—Lead nitrate is first mentioned in the *Alchymia* of Libavius. It is here termed *calx plumb. dulcis*. "Fit per aquam fortem comminuto plumbo affusam vase in aqua frigida locato. Fit instar crystallorum." Lead dissolves slowly in warm dilute nitric acid. Lead nitrate, or lead saltpetre as it is sometimes called, is prepared on the large

scale by dissolving lead-scale or litharge in hot dilute nitric acid, having a specific gravity of 1·35. The solution is evaporated until it attains a specific gravity of 1·6, and then is allowed to cool in earthenware vessels, when the salt separates out in milk-white regular octohedra exhibiting a combination of the regular dodecahedron. If a cold solution of the salt be allowed to undergo spontaneous evaporation, transparent octohedral crystals are formed (Knop). It has a specific gravity of 4·5, and on dissolving in water gives rise to a reduction of temperature. 100 parts of water dissolve, according to Kremers, as follows:—

At	0°	10°	25°	45°	65°	85°	100°
$Pb(NO_3)_2$	38·7	48·3	60·6	80·0	101·0	120·4	138·9

It scarcely dissolves in strong alcohol, and is only slightly soluble in aqueous alcohol. Its aqueous solution is precipitated by nitric acid. It has an astringent metallic taste, decrepitates when heated, detonates with brilliant sparks when thrown upon red-hot charcoal, and deflagrates when triturated with sulphur. The salt is largely used in dyeing and calico-printing, for the preparation of mordants, and for the preparation of chrome-yellow.

When the normal salt is boiled with an equal weight of lead oxide and water, crystals of a basic nitrate $Pb(NO_3)OH$ are thrown down on cooling. These are sparingly soluble in cold and more readily soluble in hot water. When gently heated it is converted into red-lead. If a solution of the normal salt be precipitated with a slight excess of ammonia, and the solution heated in a closed vessel with the addition of some of the normal salt until the smell of ammonia has almost disappeared, a basic nitrate is formed, having the composition $2Pb(NO_3)OH + PbO$. It is a white powder slightly soluble in water. When an excess of ammonia is employed, the compound $Pb(NO_3)OH + 2PbO$ is thrown down as a white powder.

381 *Phosphates of Lead.*—When common sodium phosphate is precipitated by acetate of lead, a white precipitate of normal lead orthophosphate, $Pb_3(PO_4)_2$, is formed. If a boiling solution of lead nitrate be precipitated by phosphoric acid, a glittering white crystalline precipitate of $HPbPO_4$ is produced, and the same compound is obtained in the form of crystalline needles when lead pyrophosphate is heated with water to 250°. The pyrophosphate and metaphosphate of lead are white precipitates.

The following minerals are lead phosphates and arsenates isomorphous with apatite:—

Pyromorphite, $Pb_3(PO_4)_2 + Pb_2\begin{cases}PO_4\\Cl\end{cases}$,

Polysphærite, $(Pb,Ca)_3(PO_4)_2 + (Pb,Ca)_2\begin{cases}PO_4\\Cl\end{cases}$,

Mimetesite, $Pb_3(AsO_4)_2 + Pb_2\begin{cases}AsO_4\\Cl\end{cases}$, and

Kampylite, $Pb_3\,[(As,P)O_4]_2 + Pb_2\begin{cases}(As,P)O_4\\Cl\end{cases}$.

These usually contain a portion of their chlorine replaced by fluorine.

Borates of Lead.—If boron trioxide and lead oxide be fused together in the proportion of 2 molecules of the former to 3 of the latter, a yellowish soft glass is obtained, which softens when exposed to the action of hot oil. If double the weight of boron trioxide be employed, the glass obtained is harder and less coloured, and if three times the weight be used a colourless glass is obtained, which possesses the hardness of flint-glass, and which refracts light much more powerfully.[1] When a lead salt is precipitated with borax, a compound having the composition $Pb_2B_6O_{11} + 4H_2O$ is formed, and this when warmed with strong ammonia is converted into a heavy white powder having the composition $PbB_2O_4 + H_2O$, which again, when boiled with a solution of boric acid, yields an amorphous powder of $PbB_4O_7 + 4H_2O$.

Lead and Carbon and Silicon.

382 *Carbonates of Lead.—Normal Lead Carbonate,* $PbCO_3$, occurs as cerussite or white carbonate of lead in rhombic crystals isomorphous with arragonite, and also as pseudomorphs of galena and lead sulphate. The same compound is formed by precipitating a cold solution of lead acetate by ammonium carbonate (Berzelius), or by passing carbon dioxide into a dilute solution of sugar of lead (Rose). Cerussite forms colourless transparent lustrous crystals, having a specific gravity of 6·46, whilst the precipitated carbonate has a specific gravity of 6·43. It is scarcely soluble in water; 1 part dissolving in 50,500 parts of water at the ordinary temperature, but in presence of ammoniacal

[1] Faraday, "On the Manufacture of Optical Glass." *Phil. Trans.* 1830, 1.

salts it is somewhat more soluble (Fresenius). A solution of carbon dioxide in water also dissolves it slowly.

Lead forms several basic carbonates, amongst which *white-lead* is the most important, since it is manufactured on a very large scale. In the pure state this compound consists of $2PbCO_3 + Pb(OH)_2$, but the commercial product usually contains the normal carbonate in addition.

White-Lead has long been known, being called ψιμύθιον by Theophrastus. The process of manufacture as described by him consisted in the action of vinegar on lead, the material formed being scraped off after a time from the surface of the metal. Pliny mentions the same subject under the name of *cerussa* and describes the above method of manufacture. He also states that it may be obtained by dissolving lead in vinegar and evaporating to dryness. Thus it would appear that the difference between white-lead and sugar of lead was not known. The Latin Geber describes the manufacture as follows: "plumbum ponendo super vaporem aceti fit cerussa," a description which accords with the method employed even up to the present day. For some time white-lead was supposed to be a compound of calx of lead with vinegar, and it was not until 1774 that Bergman showed that white-lead contains lead calx and fixed air and gave to it the name of "luftsaurer blei-kalk" or "calx plumbi ærata."

The oldest process for the manufacture of white-lead is known as the *Dutch process*. In this method conical glazed earthenware pots, 8 inches wide, are filled to one-fourth of their depth with malt vinegar. At one-third of the height of the pot from the bottom are three projecting points on which a cross-piece of wood is laid, and on this are placed vertically a number of leaden plates rolled up into a spiral, and the whole covered with a leaden plate. The pots are then placed under a shed in rows upon horse-dung or spent tannery-bark covered with boards, another layer of dung or decomposing bark laid upon the boards, and on this another row of pots, many rows of pots being thus placed above one another, and the whole covered by the tan or dung. By the slow oxidation of the dung, heat is evolved, which assists the evaporation of the vinegar and causes basic lead acetate to be formed, and this in contact with the carbon dioxide evolved from the putrefaction of the organic matter is converted into white-lead. In the course of from 4 to 5 weeks the greater portion of the lead is converted into white-lead, the

change taking place from without inwards. The white-lead is then detached, ground into a fine paste whilst moist, washed well to free it from adhering acetate, and dried in small round pots. Unwashed white-lead contains a considerable quantity (from 2 to 12 per cent.) of the normal acetate.

According to the *German method* of manufacture, plates of lead are hung up in wooden boxes placed in heated chambers containing a stratum of acetic acid, or the plates are suspended in heated chambers having their floors covered with tan and acetic acid.

The *French method*, introduced by Thénard, and the *English method*, suggested by Benson, do not furnish a white-lead which possesses the same covering power as that prepared by the other methods. The process in these cases consists in passing carbon dioxide through a solution of a basic acetate of lead, obtained by boiling a solution of sugar of lead with litharge.

Another method, which yields a white-lead of excellent covering power is the process patented by Dale and Milner. This consists in carefully grinding between millstones a mixture of litharge, or any insoluble basic lead salt, with water and sodium bicarbonate. Milner has improved upon this method by grinding a mixture of 4 parts of finely-divided litharge with 1 part of common salt and 16 parts of water. After about 4½ hours the reaction is complete. The mixture of basic lead chloride and caustic soda is then brought into a leaden vessel, well stirred with a wooden pestle and a current of carbon dioxide passed through it until the liquid is neutral. If the carbon dioxide be passed in too long the product is spoiled.[1]

White-lead is a white, earthy, heavy, amorphous powder which appears under the microscope to consist of round transparent globules of the size of from 0·00001 to 0·00004 of an inch in diameter. It was formerly supposed that the feeble covering power of the white-lead manufactured according to the French method depended upon the fact that it was crystalline. The specific gravity of that prepared by the Dutch method is somewhat greater than that prepared by the French method, and it therefore absorbs less oil or varnish and gives rise to a thicker colour.

Although it acts as a powerful poison, and is turned black by sulphuretted hydrogen, white-lead is still almost exclusively used as the basis of paint, and has been replaced only to a very small extent by zinc-white or baryta-white. This is accounted

[1] Patent No. 4.053; 22nd November, 1875.

for by the fact that it possesses a much greater covering power and is much more opaque than is either of the other two.

White-lead is often mixed with heavy-spar and gypsum. A mixture of equal parts of white-lead and barium sulphate is known as *Venetian white*, whilst *Hamburg white* is a mixture of 1 part of white-lead to 2 of barium sulphate, and *Dutch white* of 1 part to 3 of barium sulphate. The amount of this admixture may be readily ascertained by treating a weighed portion of the powder with warm dilute nitric acid, when the barium sulphate remains behind. The estimation may also be made by igniting and heating to the point of fusion and weighing the residue; the amout of sulphate can then be readily calculated inasmuch as white-lead when heated loses the whole of the carbon dioxide leaving lead monoxide behind. An average sample of white lead loses 14 per cent of its weight on ignition. Hence if a sample loses less than this weight it is easy to calculate how much pure white-lead it contains.

Lead carbonate forms a constituent of the following minerals: cromfordite or phosgenite, $PbCO_3 + PbCl_2$; leadhillite, $3PbCO_3 + PbSO_4$, and lanarkite, $PbCO_3 + PbSO_4$.

Lead Cyanide, $Pb(CN)_2$, is obtained as a white powder when a solution of a normal lead salt is mixed with potassium cyanide. It is not soluble in the cyanides of the alkali metals, and is decomposed on the addition of an acid. When heated in a closed vessel a mixture of lead and charcoal remains behind which, if it has not been too strongly heated, is pyrophoric.

Lead Cyanate, $Pb(CNO)_2$, is obtained by mixing solutions of a cyanate and of a soluble lead salt. A dense white precipitate is thrown down, which soon assumes the form of slender needles like chloride of lead. It is soluble in boiling water.

Silicates of Lead.—Silica fuses with lead oxide to form a yellow glass. Glass formed of equal parts of lead oxide and silica does not become dull when it is exposed to the action of sulphuretted hydrogen, but if 8 parts of the glass are fused with 1 part of potash, the glass produced becomes tarnished on exposure.[1] Lead silicate forms a constituent of flint-glass.

Poisonous Action of Lead Salts.

383 The soluble lead salts are strongly poisonous and are employed in medicine. The normal or basic acetate given in doses

[1] Faraday, "On the Manufacture of Optical Glass." *Phil. Trans.*, 1830, 1.

from 0·3 to 0·6 gram. produces acute symptoms of lead poisoning which often end fatally.

When taken for a considerable time in small doses, especially in the case of the oxides and carbonates, chronic lead poisoning is observed. The disease called painters' colic is the chronic form of poisoning by carbonate of lead. The symptoms of chronic lead poisoning are pain in the abdomen, constipation, loss of appetite, thirst, and general emaciation followed by nervous prostration known as lead-palsy, epileptic fits, and total paralysis.

A very characteristic phenomenon accompanying chronic lead poisoning is the appearance of a blue line at the edges of the gums due to the deposition of lead sulphide. This line is often seen in the case of house-painters and the workmen engaged in white-lead works, as well as those occupied in manufactures in which white-lead is employed, as, for instance, in the manufacture of glazed cards. On the other hand, plumbers, who only handle metallic lead, which is not poisonous, are not subject to the disease.

The Action of Water upon Lead.

384 As lead acts as a cumulative poison, its salts produce serious results if taken into the system even in very minute quantities for a length of time. Drinking-water is often collected in lead-lined cisterns and passes through leaden pipes, and as water under certain circumstances can take up notable quantities of lead it becomes of great importance to determine the conditions under which the solvent action is exerted. A fresh bright surface of lead does not tarnish in a perfectly dry atmosphere or when sealed up in a vessel filled with pure distilled water from which all air has been expelled by boiling. If, however, it be exposed to the united action of air and water the lead is oxidised to hydroxide which dissolves. After a time, this is converted by the action of the atmospheric carbon dioxide into an insoluble basic carbonate. Lead hydroxide is then again formed, and thus the corrosive action may be continued.

Potable waters always contain a certain amount of salts in solution and the corrosive action on lead depends upon the nature and quantity of the salts thus present. The ammoniacal salts act most prejudicially on water in this respect; this is especially the case with ammonium nitrate, which greatly assists

the oxidation and solution of the lead. Other nitrates do not, however, appear to possess this power, and sulphates, phosphates carbonates and silicates either retard or altogether prevent this action, and hence water containing carbonic acid in solution or temporarily hard water consisting of a solution of calcium carbonate in carbonic acid gives rise to the formation of insoluble basic lead carbonate; if, however, an excess of carbon dioxide is present, this is dissolved, the water taking up lead in considerable quantity.

The following table contains the results of experiments on the solubility of lead in water containing various salts in solution. Bright plates of lead having a surface of 5,600 sq. mm. were placed in flasks which contained 500 cc. of water in which the salts were dissolved, the saline solutions being allowed to act upon the lead for different periods of time:[1]—

Salt.	Grams per Litre.	Milligrams per Litre of Lead dissolved		
		24 hours.	48 hours.	72 hours.
NH_4NO_3 . .	0·02	13·0	—	25·0
" . .	0·04	15·0	—	32·0
KNO_3 . . .	0·02	2·0	2·0	—
$NaNO_3$ . . .	0·05			
KNO_3 . . .	0·07	—	—	0·5
K_2SO_4 . . .	0·50			
KNO_3 . . .	0·045	—	—	0·3
K_2CO_3 . . .	0·308			
$CaCl_2$ . . .	0·25	0·5	0·5	0·5
NH_4NO_3 . .	0·02	—	—	1·8
$CaCl_2$ . . .	0·06			
Na_2SO_4 . . .	0·020			
K_2CO_3 . . .	0·040	—	—	0·1
$CaCl_2$ . . .	1·100			
K_2CO_3 . . .	0·31	—	—	0·2
Distilled water with carbon dioxide at ordinary pressure		3·0	—	3·0
Ditto with carbon dioxide at a pressure of about 6 atmospheres . . .		14·8	24·0	—
Distilled water . . .		2·0	2·0	3·0

[1] Muir, *Proc. Man. Phil. Soc.* 1875, 31; *Journ. Chem. Soc.* 1877. See also Carnelley and Frew, *J. Soc. Chem. Ind.* 1888, **7**, 15, 78; Reichardt, *Arch. Pharm* 1887 [3], **25**, 858, 1059; Müller, *J. pr. Chem.* 1887 [2], **36**, 317.

Detection and Estimation of Lead.

385 The soluble lead salts possess a sweet astringent taste, whence the name sugar of lead has been given to the acetate, and are very poisonous. These two properties of the lead compounds have been long known, and it became in early times of importance to detect the presence of lead, inasmuch as the compounds of this metal were largely employed for a great variety of purposes. Thus, for instance, the Romans were in the habit of boiling their poor wines in leaden vessels, and Pliny mentions the fact that the point at which the wine becomes sour can be detected by hanging a strip of lead in it and then observing when this undergoes any change in its appearance. In later times the addition of metallic lead to a cask of sour wine was said to render it drinkable. At a still later date, litharge appears to have been employed for the same purpose. It was observed that the treatment of wine with lead could be detected by the addition of sulphuric acid, and in 1707 Zeller suggested that an extract of orpiment and lime-water (containing, therefore, sulphide of calcium) was an invaluable test for the presence of lead, inasmuch as this liquid turns all lead salts black. This reaction led to the simultaneous suggestion, in 1787, by Fourcroy and Hahnemann of the application of water acidified with hydrochloric acid and then saturated with sulphuretted hydrogen for the detection of lead, and thus the most important reagent which we now employ in analytical chemistry for the detection and separation of the metals was introduced.

Potable water may be examined in this way for lead by passing sulphuretted hydrogen through water slightly acidified by hydrochloric acid. It is, however, to be remembered that many other metals, such as mercury, copper, and bismuth, also produce black precipitates. The absence of these metals must, therefore, be ascertained before the presence of lead can be certainly proved. Black lead sulphide can be readily distinguished from other black sulphides insoluble in dilute hydrochloric acid by dissolving it in warm dilute nitric acid and filtering the solution; on addition of sulphuric acid to the filtrate, from which the excess of acid should be removed by evaporation, a white precipitate of lead sulphate is obtained. By means of this reaction lead may be detected in the presence of all the other metals and separated from them. Lead com-

pounds, heated before the blowpipe on charcoal, yield a malleable bead of lead readily soluble in warm nitric acid, and the solution yields a precipitate with sulphuric acid.

Another characteristic test for lead is, that when present in not too dilute solution, a crystalline precipitate of the chloride is obtained on the addition of hydrochloric acid. This is soluble in boiling water, and separates out on cooling in crystalline needles. Potassium chromate gives in the presence of free nitric acid, a fine yellow precipitate of chrome yellow, $PbCrO_4$. In order to detect small quantities of lead in presence of large masses of organic matter, as is necessary in cases of lead poisoning, the mass is evaporated to dryness with sodium carbonate, the residue ignited gently, and the carbonised mass rubbed fine and carefully lixiviated, when small glittering heavy spiculæ of metallic lead remain behind. These can be examined as already described.

Lead is easily determined quantitatively in the form of sulphate, being precipitated with dilute sulphuric acid and then washed with strong alcohol. For certain separations lead is also determined as the chloride. In this case the solution is precipitated by hydrochloric acid, evaporated on a water-bath, and the concentrated liquid treated with a mixture of ether and alcohol, in which the chloride is insoluble. Lead carbonate and lead oxalate are also occasionally used for the estimation of lead, and these precipitates are then converted by ignition into lead oxide.

Lead compounds impart a pale tint to the non-luminous gas-flame and this exhibits characteristic lines in the green (Werther). The spark spectrum of lead contains a large number of lines between the orange and violet. The brightest and most characteristic of these is a violet line (4058), a somewhat less bright one in the green (5608), and a fainter one lying near the less refrangible of the "D" lines of Fraunhofer (5875) (Lecoq de Boisbaudran).

The most accurate determinations of the *atomic weight of lead* are those of Stas.[1] By the conversion of pure lead into the nitrate he obtained the number 204·85 as a mean of ten experiments. Six other experiments in which the nitrate was converted into the sulphate gave the number 204·86 (O = 15·88).

[1] *Bull. Roy. Acad. Belg.* [2], **10**, 298.

THORIUM = 230·7.

386 In the year 1815 Berzelius believed that he had found a new earth in several Swedish minerals, to which he gave the name of thoria, but on further examination the substance turned out to be basic phosphate of yttrium. On the other hand, in 1828,[1] he discovered a distinct earth in a mineral from the island of Lövön, in Norway, now termed thorite, and to this the name of thoria was given, as it agreed in many of its properties with the substance previously so named. Besides being found in thorite, this substance was discovered in other rare minerals; thus by Wöhler in pyrochlor, by Bergman and others in orangeite, and by Karsten in monazite, a phosphate of cerium and lanthanum which contains from 0·5 to 1·5 per cent. of thoria. Another source of thoria is the mineral euxinite from Arendal, in which this earth was discovered by Mosander and Chydenius, and it has also been found in Norwegian granite.[2]

The following table gives the composition of some of these minerals:

Thorite from Lövön.		Orangeite from Langesundfiord.		Monazite from Ilmengebirge.	
SiO_2	19·31	SiO_2	17·76	P_2O_5	28·50
ThO_2	58·91	ThO_2	73·80	ThO_2	17·95
UO_3	1·64	PbO	1·18	SnO_2	2·10
Fe_2O_3	3·46	CaO	1·08	Ce_2O_3	26·00
Mn_2O_3	2·43	H_2O	6·45	La_2O_3	23·40
CuO	2·62			MnO	1·86
MgO	0·36		100·27	CaO	1·68
K_2O	0·15				
Na_2O	0·11				101·49
PbO	0·82				
SnO_2	0·01				
Al_2O_3	0·06				
H_2O	9·66				
	99·54				

Thorium also occurs in other minerals containing the metals of the cerium group, as gadolinite and orthite. In one of these

[1] *Pogg. Ann.* 1829, **16**, 385. [2] Phipson, *Chem. News*, 1896, **73**, 145.

minerals Bahr believed he had found another new metal to which he gave the name wasium, but he afterwards convinced himself that this substance is identical with thorium.[1]

Metallic Thorium is obtained by heating potassium thorium chloride with sodium in an iron cylinder. Thus prepared it forms microscopic hexagonal tablets, having the colour of nickel and giving a silver-white streak. It has a specific gravity of 11·0, and takes fire when heated in the air, burning with a bright flame; dissolves with difficulty in hydrochloric acid, and is not attacked by aqueous alkalis, but is readily soluble in nitric acid and aqua regia.[2]

At the present time thorium compounds are prepared on the manufacturing scale, as they form the chief constituent of the mantles employed for the Welsbach incandescent gas-burner. Thorite is the most convenient raw material, but is not found in sufficient quantity, and the crude material mostly employed is the Brazilian monazite sand. The method adopted in the latter case is at present kept secret.

387 *Thorium Dioxide* or *Thoria*, ThO_2, is obtained from thorite or orangeite by heating the powdered mineral with a slight excess of sulphuric acid and a little water; the dried mass is powdered, heated to remove excess of sulphuric acid, and the residue carefully dissolved in six to seven parts of ice water. The solution is filtered from silica, and heated to the boiling point with ammonia. The precipitated hydroxides are washed by decantation, dissolved in hydrochloric acid and precipitated with oxalic acid, the precipitate well washed by decantation, and ignited. The thoria thus obtained still contains ceria, yttria and a little manganese. To obtain pure thoria the product is again dissolved in sulphuric acid, the excess of sulphuric acid removed by careful heating, the powdered salt dissolved in ice cold water, and the temperature of the solution allowed to rise gradually to 20°. A hydrated sulphate of thorium then separates out as an insoluble precipitate, the other metals remaining in solution, and by repeating the process several times the thorium sulphate may be obtained perfectly pure. It is then precipitated by ammonia and the hydroxide thus obtained ignited.[3]

Pure thoria is a snow-white powder, which may be obtained

[1] *Annalen*, 1864, **132**, 227.
[2] Nilson, *Ber.* 1882, **15**, 2519, 2537; 1883, **16**, 153.
[3] Krüss and Nilson, *Ber.* 1887, **20**, 1665.

in quadratic crystals isomorphous with those of cassiterite and rutile by heating the amorphous powder with borax in a porcelain furnace. These possess a specific gravity of 10·2 and only dissolve in sulphuric acid on long continued boiling. As already mentioned thoria forms the chief constituent of the Welsbach incandescent mantles, the other and smaller constituents consisting of more basic oxides, that of cerium being usually employed.

Meta-thorium Oxide, Th_3O_5, is obtained by igniting the oxalate, and its peculiar deportment with volatile acids explains the fact that Bahr believed this to be the oxide of a new metal. If it be treated with hydrochloric acid or nitric acid no apparent action takes place, but if the excess of acid be evaporated on the water-bath, a brownish semi-transparent residue is left, and this dissolves in water to form a translucent opalescent liquid which appears milk-white in reflected light, and from which a small quantity of nitric or hydrochloric acid precipitates the oxide. If the solution be precipitated with ammonia and the precipitate dried at 100°, a compound having the composition $Th_4O_7(OH)$ is obtained and this is insoluble in acids.[1]

SALTS OF THORIUM.

388 The salts of thorium are colourless, and those which are soluble possess a strongly astringent taste.

Thorium Fluoride, ThF_4, is obtained in the form of a heavy white insoluble powder by dissolving the hydroxide in hydrofluoric acid and evaporating to dryness. If a solution of a thorium salt be precipitated by a soluble fluoride, a gelatinous precipitate of ThF_4+4H_2O is thrown down.

Potassium Thorofluoride, $K_2ThF_6+4H_2O$, is obtained by boiling the hydroxide with potassium fluoride and hydrofluoric acid, in the form of a heavy black powder. When a solution of the chloride is precipitated with acid potassium fluoride the compound $K_2ThF_6+4ThF_4+H_2O$ is thrown down.

Thorium Chloride, $ThCl_4$.—This is obtained by heating the oxide mixed with carbon in a current of chlorine. It melts at a white-heat and sublimes in white shining tables, its vapour density being 12·42, corresponding to the above formula. It deliquesces on exposure, and its solution may be obtained by

[1] Cleve, *Bull. Soc. Chim.* 1874, **21**, 115.

dissolving the hydroxide in hydrochloric acid. The strongly concentrated solution solidifies to a fibrous crystalline mass, which on heating emits hydrochloric acid. It forms with the chlorides of the alkali metals easily soluble double salts, as $KCl+2ThCl_4+18H_2O$.

Thorium Sulphide, ThS_2.—The metal burns in sulphur vapour with great brilliancy forming a yellow powder, which exhibits a metallic lustre under the burnisher, and has probably the above composition (Berzelius). When carbon bisulphide vapour is passed over thorium dioxide heated to redness it yields the *oxysulphide*, ThOS, as a light brown substance.[1]

Thorium Sulphate, $Th(SO_4)_2$, is obtained by dissolving the oxide in hot concentrated sulphuric acid, or by rubbing up powdered thorite or orangeite to a paste with sulphuric acid, and heating the mixture to 500° until all the excess of sulphuric acid is driven off. The mass is then treated with cold water, and boiled; a crystalline precipitate remains, and this may be purified by repeated solution in cold water and reprecipitation by boiling. If the solution be allowed to evaporate at the ordinary temperature, transparent monosymmetric crystals of $Th(SO_4)_2+9H_2O$ are deposited, whereas above 43° a hydrate with $4H_2O$ is formed. Several other hydrates have also been obtained.[2] Thorium sulphate forms double salts with the sulphates of the alkali metals. $Th(SO_4)_2+2K_2SO_4+2H_2O$ crystallises in regular prisms, which are easily soluble in water, but do not dissolve in a solution of potassium sulphate.

Thorium Nitrate, $Th(NO_3)_4+12H_2O$, is a very soluble salt, crystallising in large deliquescent tables.

The *phosphate* is a precipitate insoluble both in water and phosphoric acid.

Thorium Carbide, ThC_2, is prepared by heating thoria with sugar charcoal in the electric furnace, and forms a crystalline mass which is only slightly affected by concentrated acids but readily dissolves in dilute acids and is decomposed by water with evolution of a mixture of methane, ethylene, acetylene and hydrogen.[3]

[1] Krüss, *Zeit. anorg. Chem.* 1894, **6**, 49.
[2] Roozeboom, *Zeit. Phys. Chem.* 1890, **5**, 198.
[3] Moissan, *Compt. Rend.* 1896, **122**, 573.

Detection and Estimation of Thorium.

389 The compounds of this metal give no characteristic blowpipe or flame-reaction. The alkalis and ammonium sulphide precipitate from its solutions the hydroxide insoluble in excess, and the carbonates give rise to a precipitate of a basic carbonate, which dissolves in an excess of the reagent. Ammonia produces no precipitate in this solution as it does in the corresponding one containing zirconium. Another characteristic property of thorium is its reaction with potassium sulphate, and especially the fact that the thiosulphate is thrown down from thorium solutions on addition of potassium thiosulphate, a reaction by which this metal may be separated from the metals of the cerium group. In order to separate it from titanium, niobium and tantalum, ammonium oxalate is added to the solution when the thorium alone is precipitated. Thorium can be separated from zirconium by throwing down both metals as oxalates by ammonium oxalate, and then adding an excess of oxalic acid when the zirconium oxalate dissolves completely, leaving behind the oxalate of thorium. Thorium is determined quantitatively as the oxide obtained by igniting the precipitated hydroxide.

The *atomic weight* of thorium was determined by several chemists without concordant results. Thus Berzelius[1] found 235·5, and Delafontaine[2] the number 229·7 as the mean of several well-agreeing analyses of the sulphate. Cleve, by the same method, obtained the number 232·6, whilst analyses of the oxalate yielded him the number 232·2. On the other hand, Krüss and Nilson by analysing the carefully purified sulphate obtained the number 230·7 as a mean of several well-agreeing experiments (O = 15·88).[3]

[1] *Pogg. Ann.* 1829, **16**, 385. [2] *N. Arch. Ph. Nat.* **18**, 343.
[3] *Ber.* 1887, **20**, 1665.

GROUP V.

Nitrogen.	Niobium.
Phosphorus.	Antimony.
Vanadium.	Tantalum.
Arsenic.	Bismuth.

390 As in the preceding group (p. 638), the members of the two sub-groups resemble one another, especially in chemical properties, very closely, although they differ in certain respects.

Many chemists include certain of the rare earth metals in this group (didymium, erbium), but so little is known of the real relations of these substances, that it is by no means certain that they actually belong to it.

All the elements of the group are characterised by the formation of acid-forming oxides of the empirical formula R_2O_5, the acidity of the resulting acid diminishing as the atomic weight of the element rises. Thus the salts of bismuthic acid are only stable in the presence of a large excess of alkali, whereas the vanadates, arsenates, &c., are well-defined and stable salts.

The three elements, vanadium, niobium, and tantalum, which together with nitrogen, belong to the even series, combine so readily with oxygen that it is extremely difficult to obtain them in the free state. They all have a metallic appearance, and only melt at a very high temperature. They moreover do not form volatile compounds with hydrogen or the alcohol radicals.

The elements of the odd series, phosphorus, arsenic, antimony, and bismuth, on the other hand, are easily reduced from their oxides, melt at moderate temperatures, and can all be volatilised. They exhibit in their external characteristics the gradual passage from a well-marked non-metallic element (phosphorus) to a well-defined metal (bismuth), and the same progression is also to be traced in their chemical properties (p. 5). Thus the lower oxide of phosphorus, of the empirical formula P_2O_3, is the anhydride of a well-marked acid, but does not yield salts, even with strong acids. Arsenious oxide yields unstable salts with strong acids, such as sulphuric acid; the corresponding oxide of antimony yields more stable salts, and the trioxide of bismuth is entirely devoid of acid-forming properties, and reacts with

acids to form a whole series of salts of the type RX'_3. The same increase in basicity is observable in the sulphides of these elements, and, as already remarked, in the pentoxides.

Phosphorus, arsenic and antimony, as well as nitrogen, yield very characteristic volatile hydrogen compounds, but no analogous derivative of bismuth has yet been prepared. They all, however, form organo-metallic derivatives.

The group is further characterised by the large number of oxides and halogen derivatives formed by its members. In many of these the valency of the elements varies considerably. They are all distinguished by a tendency to form two series of compounds of the types RX'_3 and RX'_5 (or $R_2X''_3$, $R_2X''_5$), but, in addition to this, some of them also act as dyads and tetrads. Thus nitrogen is divalent in nitric oxide, NO, and tetravalent in nitrogen peroxide, NO_2, whilst vanadium is tetravalent in the tetrachloride, VCl_4.

The elements, nitrogen, phosphorus and arsenic, and their chief derivatives, have already been described in vol. i.

VANADIUM, V = 50·9.

391 In 1801, Del Rio pointed out the existence of a new metal in a lead ore found at Zimapan, in Mexico,[1] and gave to it the name Erythronium, from the fact that its salts became red when heated with acids. In 1805, Collet-Descotils,[2] expressed his opinion that this supposed new metal was an impure oxide of chromium, and Del Rio accepted this conclusion as correct. In 1830, Sefström[3] described a new metal which he found in the celebrated iron of Taberg, and for this he proposed the name of Vanadium, from *Vanadis*, a cognomen of the Scandinavian goddess Freia. In the same year Wöhler[4] showed that Del Rio's discovery was a true one, and that the Zimapan ore was a vanadate of lead. Unable to carry out the further investigation of the new metal, Sefström handed the materials, amounting only to a few grams, to Berzelius, and in 1831 this chemist[5] published the results of an exhaustive investigation on the subject, in which he described a large number of vana-

[1] *Gilbert's Ann.* 1801, **71**, 7.
[2] *Ann. Chim. Phys.* 1805 [1], **53**, 260.
[3] *Pogg. Ann.* 1830, **21**, 48.
[4] *Pogg. Ann.* 1831, **22**, 1.
[5] *Loc. cit.*

dium compounds, and came to the conclusion that vanadium closely resembled chromium and molybdenum, yielding, like these metals, an acid-forming trioxide. This view was universally adopted until the year 1867, when Roscoe showed that the substance supposed by Berzelius to be vanadium was, according to the mode of its preparation, either an oxide or a nitride; that the volatile trichloride of Berzelius contained oxygen, and possessed a composition analogous to that of phosphorus oxychloride; and that the metal, instead of belonging as was supposed, to the chromium group, was a member of the antimony group and intimately connected with the nitrogen, phosphorus, and arsenic family.

Vanadium is an extremely rare substance, forming an essential constituent of only a few scarce minerals. Traces of this element, are, however, tolerably widely distributed throughout terrestrial matter, and it exists in the sun.

The principal vanadium minerals are vanadinite, or lead vanadate, $3Pb_3(VO_4)_2 + PbCl_2$; dechenite, $(PbZn)(VO_3)_2$; descloizite, $Pb_2V_2O_7$; pucherite, $BiVO_4$; psittacinite, $(PbCu)_3(VO_4)_2 + 3Cu(OH)_2 + 6H_2O$; volborthite, $(CuCa)_3(VO_4)_2 + H_2O$; roscoelite, $4AlVO_4 + K_4Si_9O_{20} + H_2O$; mottramite, $(PbCu)_3(VO_4)_2 + 2(PbCu)(OH)_2$. Mottramite has been found in tolerable quantity in the copper-bearing beds of the Keuper, worked at Alderley Edge and Mottram St. Andrews in Cheshire, and it is from this source that the vanadic acid of commerce was obtained, it having been for some time manufactured on the large scale by the Magnesium Metal Company at Patricroft near Manchester. Traces of vanadium have also been found in a large number of clays, in trap and basalt, in certain iron ores and cast-iron, in larger quantities in the slag from the basic steel process at Creuzot, in certain coals and lignites, and also in soda-ash, as well as in sodium phosphate.

Extraction and Preparation of the Vanadium Compounds.—The methods adopted for the preparation of vanadium from its various sources depend upon the fact, discovered by Sefström, of the existence of an insoluble ammonium metavanadate, which by repeated crystallisation can be obtained free from phosphorus and other impurities.

In order to prepare vanadium salts from mottramite, the keuper-sandstone, which contains the mineral deposited as a film on the surface of the grains of sand, is digested with strong hydrochloric acid, the acid liquor drawn off and the

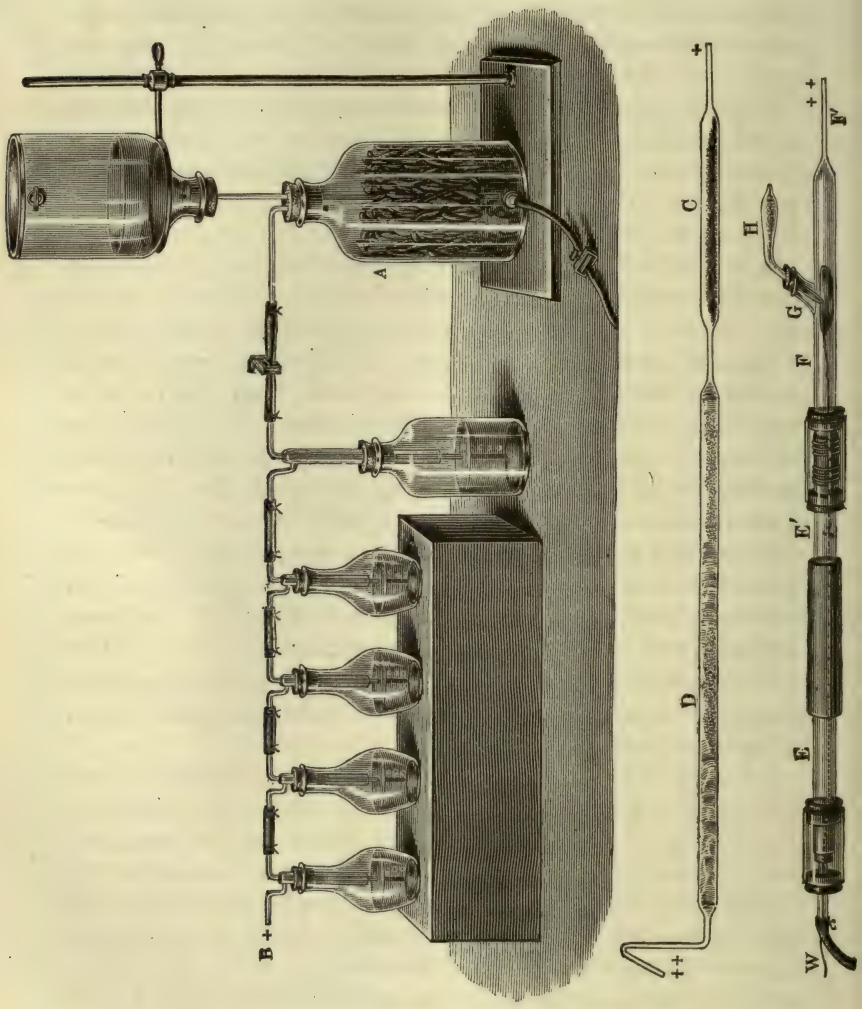
sand well washed with water. The acid solution, together with the washings, after concentration, is evaporated down with an excess of sal-ammoniac, when ammonium metavanadate separates out, and this is repeatedly crystallised to free it from copper and iron. The crude ammonium metavanadate is then gently roasted in porcelain, by which means the vanadium pentoxide is obtained in a tolerably pure condition. In order to purify this it is suspended in water and ammonia gas passed into the liquid. A solution of ammonium vanadate is thus formed and separated by filtration from the residue containing silica, phosphates, &c., and then crystallised by evaporation in platinum vessels; the pentoxide obtained by several repetitions of this treatment is free from phosphorus.

392 *Metallic Vanadium.*—Berzelius obtained brilliant metallic scales by heating the oxytrichloride in an atmosphere of ammonia. These do not, however, consist of metallic vanadium, but of vanadium nitride. An impure metal containing a large amount of carbon is obtained when vanadium pentoxide is heated with carbon in the electric furnace. The mass thus formed has a specific gravity of 5·3.[1] The only method which has been found possible for obtaining pure metallic vanadium is the reduction of the dichloride in perfectly pure hydrogen. Although this process appears simple enough, there is no metal more difficult to prepare than vanadium. This arises from the fact that whilst vanadium is stable at the ordinary atmospheric temperatures, it absorbs oxygen at a red heat with the greatest avidity, so that every trace of air or moisture must be excluded during its preparation. Moreover, the dichloride itself cannot be readily obtained in quantity.

For the purpose of reducing the metal the apparatus shown in Fig. 160 is employed. It consists of a hydrogen generator (A) yielding a stream of hydrogen which can be kept constantly passing through the wash-bottles, day and night for a week at a time, by occasionally adding fresh acid to the upper bottle and drawing off the zinc sulphate solution from the lower bottle by the caoutchouc tubing. The first wash-bottle contains a solution of lead acetate, the second one of silver nitrate, and the three others contain boiled sulphuric acid. In order to remove any trace of oxygen which may have accompanied the hydrogen, arising either from diffusion or from air absorbed in the dilute acid used, a tube (CD) is attached to

[1] Moissan, *Compt. Rend.* 1893, **116**, 1225.

the last washing-bottle; the first portion of this tube contains a quantity of platinum sponge (C) which is heated to redness during the whole time the hydrogen is passing through the apparatus, whilst the further portion of the tube (D) is filled



with phosphorus pentoxide and plugs of cotton-wool. The greatest care must be taken to have all caoutchouc stoppers and joints made as tight as possible with copper-wire and paraffin. At right angles to the drying tube (CD) is placed the reducing

arrangement shown in the lower part of the drawing. This consists of a porcelain tube (E E′) placed in a Hofmann's furnace and protected in the central portions, where it is heated, by an outer casing of sheet-iron. The porcelain tube is connected with the hydrogen apparatus by means of the wide glass tube (F F′) provided with the tubulus (G) and narrowed down to join the drying tube at F′. The joint between the porcelain and glass tubes is made of seamless caoutchouc, well wired and covered by an outer short glass cylinder, the space between the tubes and the cylinder being filled either with mercury or fused paraffin, and a similar joint is placed at the further end of the porcelain tube.

The introduction of the anhydrous dichloride without exposure to the air is effected by means of the tubulus (G), the dichloride being contained in the bent tube (H) in which it was prepared and sealed up in hydrogen. After the whole arrangement has been set up, the platinum boat being in position, as shown in the figure, hydrogen is allowed to pass through the apparatus for twelve hours to dry it completely and clear out the air; the caoutchouc stopper of the tubulus is then withdrawn and the end of the tube containing the dichloride cut off, and the tube and stopper quickly replaced, so that the crystals lie in the horizontal portions of the tube. The bent tube is next so turned in the stopper that the crystals of dichloride fall out and are collected in the platinum boat placed below. This boat, charged with dichloride, is then drawn into the centre of the porcelain tube by means of the platinum wire, the end of which (W) passes tightly through a small hole in the caoutchouc tube at the end of the apparatus. As soon as the boat is in position, the wire is cut off short at the end of the glass tube, a proper joint made, and an exit tube attached dipping under sulphuric acid.

Before the porcelain tube is heated, the caoutchouc stopper of the tubulus is surrounded by a bath of paraffin and the hydrogen is allowed to bubble through for six hours. The temperature of the porcelain tube is then gradually raised to the highest point (a bright red-heat), which the Hofmann's furnace will yield, and kept constant until the reduction is complete. Torrents of hydrochloric acid gas at once come off, and the process must be continued for some hours after the last trace of acid can be detected in the hydrogen. The process lasts from forty to eighty hours, according as the quantity of dichloride employed varies from 1 to 3 or 4 grams.

Metallic vanadium prepared by reduction from the dichloride in hydrogen is a light whitish-grey coloured powder, which under the microscope reflects light most powerfully, and appears as a brilliant crystalline metallic mass possessing a silver-white lustre. Vanadium thus prepared oxidises but slowly in the air, nor does it decompose water at the ordinary temperature, and it may be moistened and again dried in a vacuum several times without gaining in weight. Vanadium is neither volatile nor fusible when heated to redness in hydrogen. When the powdered metal is thrown into a flame, or rapidly heated in an excess of oxygen, it burns with brilliant scintillations. The specific gravity of vanadium at 15° is 5·5. The metal is not attacked by hydrochloric acid either when cold or hot, and neither strong nor dilute sulphuric acid acts upon the metal in the cold, but when heated with the strong acid it slowly dissolves, giving a greenish-yellow solution. Hydrofluoric acid dissolves the metal slowly with evolution of hydrogen and formation of a green solution, whilst nitric acid of all strengths oxidises it with violence, evolving nitrous fumes and forming a blue liquid. Both hot and cold solutions of caustic soda are without action on the metal, but when fused with the hydroxide, hydrogen is evolved and a vanadate formed.

When heated in an atmosphere of pure nitrogen, metallic vanadium at once absorbs this gas and is converted into the mononitride (Roscoe). It also forms an alloy with platinum.

Alloys of vanadium can be prepared in the electric furnace by reducing vanadic anhydride in the presence of the second metal or one of its oxides.[1]

COMPOUNDS OF VANADIUM.

Vanadium and Oxygen.

393 Vanadium forms five compounds with oxygen, analogous to the oxides of nitrogen, namely:

Vanadium monoxide	V_2O.
Vanadium dioxide, or hypovanadious oxide	$V_2O_2(VO)$.
Vanadium trioxide, or vanadious oxide .	V_2O_3.
Vanadium tetroxide, or hypovanadic oxide	$V_2O_4(VO_2)$.
Vanadium pentoxide, or vanadic oxide .	V_2O_5.

[1] Moissan, *Compt. Rend.* 1896, **122**, 1297.

All these oxides form salts, the three first acting only as basic oxides, the two highest both as acid-forming oxides, and as weak basic oxides. Of these the last oxide is the most important, and it and its compounds will therefore be first described.

394 *Vanadium Pentoxide*, V_2O_5.—The preparation of this oxide from mottramite has already been described. In the pure state it is best prepared by decomposing the oxychloride, $VOCl_3$, by water and fusing the residue. Vanadium pentoxide crystallises in splendid yellowish-red rhombic prisms (Nordenskiöld), which have a specific gravity of 3·35 (J. J. Watts), and dissolve in about 1,000 times their weight of water, giving a yellowish solution, which does not possess any taste but turns blue litmus-paper red. Vanadium pentoxide fuses without decomposition in absence of organic reducing matter to a red liquid, which on cooling yields brilliant transparent reddish-yellow needles, and at the moment of crystallisation exhibits the phenomenon of incandescence.

Vanadium pentoxide exists in several different modifications which differ in solubility and other properties. When it is prepared by igniting ammonium vanadate, evaporating with nitric acid and gently heating the residue, it forms a yellow hygroscopic powder, which unites with water to form hydrates containing 1, 2 and 8 molecules of water and dissolves in cold water to the extent of 8 grams per liter. When the oxide is heated for a long time at 440° or fused, it is converted into two different sparingly soluble modifications.[1]

Vanadium pentoxide acts as a weak basic oxide as well as an acid-forming oxide. Thus it dissolves in strong acids, forming red or yellow solutions yielding crystalline compounds, which separate out on spontaneous evaporation or cooling. These are termed the *vanadyl salts*, as they contain the triad radical vanadyl VO.

The Vanadic Acids and their Salts.

395 *Normal Vanadic Acid*, H_3VO_4, is not known.

Metavanadic Acid, HVO_3, was discovered by Gerland.[2] It forms a fine yellow pigment, sometimes termed vanadium bronze, and is employed in place of gold bronze. It is obtained in the

[1] Ditte, *Compt. Rend.* 1885, **101**, 698.

[2] *Proc. Manch. Lit. and Phil. Soc.*, 1873, 50.

form of brilliant scales of a golden or orange colour by boiling aqueous sulphurous acid with copper vanadate, prepared by the double decomposition of ammonium metavanadate and copper sulphate. On boiling this salt for a long time with sulphurous acid a mixture of brown and orange-yellow crystals is obtained, and on continuing the ebullition with more sulphurous acid, the brown crystals dissolve, the yellow metavanadic acid being insoluble.

Vanadium bronze may also be prepared by adding a solution of ammonium vanadate to one of copper sulphate containing excess of sal-ammoniac until a permanent precipitate is formed, and then gently heating to 75°, when the yellow scales are slowly deposited, and after a lapse of a few hours nearly the whole of the vanadium is precipitated. The larger the quantity of material employed and the slower the action takes place, the finer is the colour of the bronze.[1]

If the freshly prepared solution of copper vanadate be quickly evaporated in a flat dish, a crystalline residue is obtained which is soluble in water, and when this solution is dialysed for some days a clear solution of pure vanadic acid is obtained which remains clear when heated, and deposits the red amorphous pentoxide on evaporation.

Pyrovanadic Acid, $H_4V_2O_7$, is a brown precipitate closely resembling ferric hydrate, obtained by treating a solution of an acid vanadate with nitric acid. When air-dried it possesses the above composition. It is however unstable and loses half its water when dried over sulphuric acid (v. Hauer).

396 *The Vanadates.*—Inasmuch as Berzelius thought that vanadium dioxide was the metal, and, therefore, considered the highest oxide to be a trioxide, he likewise assumed that the vanadates corresponded to the chromates. In addition to the so-called normal salts examined by him, two other series were described by v. Hauer,[2] which, appearing to correspond to the dichromates and trichromates, received names analogous to these. After the true formula of the highest oxide of vanadium had been ascertained to be V_2O_5, it was evident that the so-called normal vanadates corresponded to the metaphosphates, and it was found possible to prepare both the ortho- and pyro-vanadates analogous to the corresponding phosphates, v. Hauer's salts becoming the tetra- and hexa-vanadates. Thus we have :

[1] *Ber.* 1876, **9**, 874.

[2] *J. pr. Chem.* 1856, **69**, 385 ; 1859, **76**, 156, 929 ; 1860, **80**, 324.

(1) Sodium Metavanadate . . . . . $NaVO_3$.
(2) Sodium Orthovanadate . . . . . Na_3VO_4.
(3) Sodium Pyrovanadate . . . . . $Na_4V_2O_7$.
(4) Sodium Tetravanadate . . . . . $Na_2V_4O_{11}$.
(5) Sodium Hexavanadate . . . . . $Na_2V_6O_{16}$.

Other polyvanadates of more complicated composition have also been described.[1]

Although the first three classes of vanadates correspond in composition to the phosphates, the order of stability of the soluble vanadates in aqueous solution differs remarkably from that of the phosphates, the metavanadates being the most stable and the orthovanadates the least stable; whereas in the phosphorus series the order of stability is the reverse of this. At a high temperature, on the other hand, the orthovanadate is the most stable, being formed when vanadium pentoxide is fused with an alkali carbonate, the meta-salt being produced when a solution of an alkali carbonate is boiled with vanadium pentoxide.

The property which serves best to distinguish the ortho- from the meta-vanadates is the colour of the respective copper salts. Copper orthovanadate possesses a blue-green colour, whilst the metavanadate is a light-yellow crystalline powder.

The alkali pyrovanadates are soluble, and can be readily obtained by fusing one molecule of vanadium pentoxide with two molecules of the carbonate of an alkali-metal, dissolving, and crystallising. They are likewise obtained by the decomposition of an aqueous solution of the corresponding orthovanadate. The pyrovanadates of the heavy metals are usually insoluble in water, and possess properties generally similar to those of the corresponding orthovanadates.

The metavanadates are usually yellow: some of them, especially those of the alkaline earths, zinc, cadmium, and lead, are converted into colourless isomeric modifications, in the solid state under water, in aqueous solution, and especially in the presence of alkali carbonates. The metavanadates of the alkali-metals are colourless, and on treatment with an acid give rise to anhydro-salts, which have a fine yellowish-red colour. The metavanadates of ammonium, potassium, sodium, barium, and lead, are but sparingly soluble in water. The other metavanadates are more soluble. The following are the pro-

[1] Carnelley, *Journ. Chem. Soc.* 1873, 323.

perties of the most important members of these three classes of vanadates.

Potassium Metavanadate, KVO_3, dissolves slowly in cold and readily in hot water, and with difficulty in caustic potash. When it is boiled with water and vanadium pentoxide, or fused with the latter, *potassium tetravanadate*, $K_2V_4O_{11} + 3H_2O$, is obtained, crystallising in broad reddish-yellow tablets. This salt is slightly soluble in cold and very easily soluble in hot water.

Sodium Orthovanadate, $Na_3VO_4 + 16H_2O$.—This salt crystallises in hexagonal prisms isomorphous with sodium orthophosphate. It has a strongly alkaline reaction, and is slowly decomposed by water in the cold, and more quickly on boiling into caustic soda and sodium pyrovanadate:

$$2Na_3VO_4 + H_2O = Na_4V_2O_7 + 2NaOH.$$

Sodium Pyrovanadate, $Na_4V_2O_7 + 18H_2O$, crystallises in large six-sided tables, is easily soluble in water, and is precipitated by alcohol from its aqueous solution in pearly scales. It fuses more easily than the orthovanadate, and is first formed in the preparation of the latter salt.

Sodium Metavanadate, $NaVO_3$, resembles the potassium salt, and is converted in a similar manner into *sodium tetravanadate*, $Na_2V_4O_{11} + 9H_2O$, which separates out in beautiful large orange-red crystals. This salt is only slightly soluble in water, but possesses such powerful colouring properties that 1 part of it is sufficient to impart a yellow tint to 200,000 parts of water. It effloresces on exposure to the air, becoming of a reddish-brown tint, and melts at a dark red-heat, solidifying to a dark red amorphous mass.

Ammonium Metavanadate, NH_4VO_3, is the most important vanadate. It is obtained by dissolving the pentoxide in an excess of ammonia and evaporating, or by precipitating with alcohol, in which it is insoluble. It forms colourless transparent crystalline crusts, and is insoluble in concentrated solution of sal-ammoniac, and accordingly is precipitated when a lump of sal-ammoniac is allowed to remain in a solution of a metavanadate or pyrovanadate:

$$Na_4V_2O_7 + 4NH_4Cl = 2NH_4VO_3 + 2NH_3 + H_2O + 4NaCl.$$

The solution of this salt becomes of a deep black tint when treated with tincture of galls, and Berzelius originally sug-

gested the use of this liquid as an ink. This ink is, however, not permanent, for letters thus written by Berzelius are now quite illegible (Wöhler). It has also been used in dyeing with aniline black, since its presence greatly facilitates the oxidation of the aniline hydrochloride on which the formation of the colouring matter depends. It is, however, no longer used for this purpose.

Ammonium Tetravanadate, $(NH_4)_2V_4O_{11}+4H_2O$, is obtained by the addition of acetic acid to a boiling solution of the metavanadate until the precipitate redissolves. The salt separates out from the yellowish-red liquid on cooling in large transparent orange-red crystals. If it be recrystallised from water containing acetic acid, splendid red crystals of *ammonium hexavanadate*, $(NH_4)_2V_6O_{16}+6H_2O$, are obtained.

Calcium Pyrovanadate, $2Ca_2V_2O_7+5H_2O$, is a white amorphous precipitate obtained by double decomposition of the corresponding sodium salt with calcium chloride. If the solution of sodium orthovanadate be precipitated by calcium chloride, the same salt is obtained mixed with calcium hydroxide, the orthovanadate being at once decomposed according to the equation:

$$Ca_3(VO_4)_2+H_2O=Ca_2V_2O_7+Ca(OH)_2.$$

Lead Orthovanadate, $Pb_3(VO_4)_2$, is a nearly white insoluble precipitate obtained by adding a solution of lead acetate to one of sodium orthovanadate. This salt occurs in nature combined with lead chloride as vanadinite, $3Pb_3(VO_4)_2+PbCl_2$ or $Pb_3(VO_4)_2+Pb_2(VO_4)Cl$. This mineral crystallises in hexagonal prisms, having a reddish-brown colour, and is isomorphous with apatite. It has a specific gravity of from 6·6 to 7·2, and frequently contains some phosphoric acid. It was found by Del Rio in Zimapan in Mexico, and occurs also at Leadhills in Scotland, in Carinthia, and in the Urals. It may be obtained artificially by fusing together lead oxide, vanadium pentoxide, and lead chloride, in the right proportions. The fused mass contains druses, in which thin needle-shaped crystals are contained. If boiled with water it falls to a crystalline powder consisting of microscopic hexagonal prisms, possessing the waxy lustre and the yellowish colour of natural vanadinite and having a specific gravity of 6·7 (Roscoe).

Lead Pyrovanadate, $Pb_2V_2O_7$, is found in South America as descloizite in rhombic crystals, which have an orange-green or

black colour, a bronze lustre, and a specific gravity of 5·839. It usually contains zinc, iron, manganese, and copper as impurities. If a solution of sodium pyrovanadate be precipitated with acetate of lead, the basic salt $Pb_5V_4O_{15}$ is thrown down as a light-yellow precipitate.

Lead Metavanadate, $Pb(VO_3)_2$, is obtained as a yellow precipitate when a solution of a metavanadate is mixed with one of lead acetate. The mineral dechenite chiefly consists of this compound, a portion of the lead however being usually replaced by zinc. It occurs together with lead ores, forming yellow, brown, or deep-red reniform masses, having a specific gravity of 5·6 to 5·8.

Lead Tetravanadate, $Pb_2V_4O_{11}$, is obtained by precipitating the corresponding potassium salt with lead nitrate, in the form of a reddish-yellow precipitate slightly soluble in water.

Copper Orthovanadate, $Cu_3(VO_4)_2 + H_2O$, occurs as the mineral volborthite, in which a part of the copper is replaced by calcium; it crystallises in small yellow or green hexagonal tables, having a specific gravity of 3·55, and is found in Thuringia and in the Urals. *Copper Pyrovanadate*, $Cu_2V_2O_7$, is a yellow crystalline precipitate, whilst *copper metavanadate* is an apple-green precipitate.

Silver Orthovanadate, Ag_3VO_4, is obtained by precipitating a freshly prepared solution of the sodium salt with silver nitrate. It is a deep orange-red coloured precipitate, which is easily soluble in nitric acid and in ammonia.

Silver Pyrovanadate, $Ag_4V_2O_7$, is a heavy yellow powder.

Silver Metavanadate, $AgVO_3$, forms a pale yellow gelatinous precipitate.

Vanadic, like phosphoric acid, yields complicated compounds with tungstates and molybdates.

The Lower Oxides of Vanadium.

397 *Vanadium Monoxide*, V_2O, is formed by the prolonged exposure of metallic vanadium to the air. It is a brown substance, which, when heated in the air, is gradually converted into the higher oxides. No salts of this oxide have been prepared.

Vanadium Dioxide, or *Hypovanadious Oxide*, V_2O_2 or VO.—In its power of uniting with oxygen vanadium even surpasses uranium,[1] and, like uranium, it can only be separated from its

[1] Peligot, *Ann. Chim. Phys.* 1842 [3], **5**, 5, and 1844 [3], **12**, 549.

last portions of oxygen with extreme difficulty. The oxide V_2O_2 is, moreover, found to enter as a radical into many compounds, so that the name vanadyl (VO) may appropriately be given to it. This substance, which was regarded by Berzelius as metallic vanadium, may be prepared by reducing the higher oxides with potassium, or by passing the vapour of vanadyl trichloride, $VOCl_3$, mixed with excess of hydrogen, through a combustion tube containing red-hot carbon.[1] Thus obtained it forms a light-grey glistening powder or a lustrous metal-like crust, having a specific gravity of 3·64. It is brittle, difficultly fusible, and conducts electricity. Heated to redness, it takes fire in the air and burns to the trioxide V_2O_3, whilst when heated in chlorine the oxychloride $VOCl_3$ is formed. It is insoluble in water, but dissolves in acids, yielding the hypovanadious salts. These may also be obtained in solution by the action of nascent hydrogen, evolved by metallic zinc, cadmium or sodium-amalgam, upon a solution made by dissolving vanadium pentoxide in hot concentrated sulphuric acid and then diluting with water. The liquid rapidly changes colour, passing through all shades of blue and green until after some time it assumes a permanent lavender or violet tint. In order to prove that this solution really contains the vanadium in the state of dioxide, a standard solution of potassium permanganate is added until a permanent pink colour is obtained and the vanadium has reached the highest degree of oxidation, when it is found that for every two atoms of metal three atoms of oxygen have been added. This solution of hypovanadious sulphate absorbs oxygen with such avidity as to bleach indigo and other vegetable colouring matters as quickly as chlorine. On allowing the neutralised lavender-coloured solution to stand exposed to the air for a few seconds, the colour changes to a deep chocolate-brown: and so rapid is the alteration of colour, when but little free acid is present, that such a lavender solution may serve as a reagent for the detection of free oxygen not inferior in delicacy to an alkaline pyrogallate. The changes in colour which the yellow sulphuric acid solution of vanadium pentoxide undergoes on reduction are exceedingly characteristic, and may be divided into eight stages, as follows:

[1] Schafarik, *Annalen*, 1859, **109**, 85.

Stage.	Colour.	Reaction.	State of Oxidation of the Metal.
I.	Yellow	Acid	Vanadic oxide (V_2O_5).
II.	Green	Acid	Vanadic to hypovanadic oxide.
III.	Bluish-green	Acid	Vanadic to hypovanadic oxide.
IV.	Blue	Acid	Hypovanadic oxide (V_2O_4).
V.	Greenish-blue	Acid	Hypovanadic to vanadious oxide (V_2O_3).
VI.	Green	Bleaches slightly	Vanadious to hypovanadious oxide.
VII.	Bluish-violet	Bleaches strongly	Vanadious to hypovanadious oxide.
VIII	Lavender or violet	Bleaches strongly	Hypovanadious oxide (V_2O_2).

Thus vanadic salts are yellow; the hypovanadic salts blue; the vanadious salts are green; and the hypovanadious salts lavender-coloured.

Vanadium Trioxide or *Vanadious Oxide*, V_2O_3, is obtained by heating the pentoxide in hydrogen, or by igniting the same oxide in a carbon crucible. It is also formed when vanadyl trichloride and hydrogen are passed through a red-hot tube, and when the pentoxide is heated in the oxyhydrogen flame.[1] It is a black powder, which may by pressure be united to form a coherent mass which conducts electricity. It undergoes oxidation when exposed to the air, not only being pyrophoric when warm, but also slowly taking up oxygen when exposed to the air at ordinary temperatures, and being converted into small dark indigo-coloured crystals of the tetroxide. It has a specific gravity of 4·7. When ignited in chlorine gas it is converted into vanadyl chloride $VOCl_3$, and vanadium pentoxide:

$$3V_2O_3 + 6Cl_2 = V_2O_5 + 4VOCl_3.$$

It is insoluble in most acids, but it may be obtained in solution by the reducing action of nascent hydrogen, evolved from metallic magnesium, on a solution of vanadium pentoxide in sulphuric acid. A green liquid is thus obtained, the further reduction observed in the case of zinc, cadmium, and sodium-amalgam not taking place in the case of magnesium. The green solution may likewise be obtained by the partial oxidation

[1] Read, *Journ. Chem. Soc.* 1894, **1**, 314.

of the lavender-coloured solution of hypovanadious oxide. If a current of air be passed through such a solution, in which the free acid has been neutralised by an excess of zinc and the remaining metallic zinc removed, the liquid attains a permanent brown colour, which on the addition of a few drops of acid turns green and the solution then contains vanadious sulphate. The vanadious salts have not been fully examined.

Vanadium Tetroxide, or *Hypovanadic Oxide*, V_2O_4.—This oxide can be prepared either by the oxidation of the dioxide in the air, or by the partial reduction of the pentoxide. It is readily converted by potassium permanganate into the pentoxide, and advantage is taken of this fact in the volumetric estimation of vanadium. It is a lustrous steel-coloured powder and dissolves in acids, forming solutions of the hypovanadic salts, which possess a bright blue colour. Solutions of these salts are also produced by the action of moderate reducing agents, such as sulphur dioxide and sulphuretted hydrogen or oxalic acid upon solutions of vanadic acid in sulphuric acid. They may also be obtained by passing a current of air through acid solutions of the hypovanadious salts until a permanent blue colour is attained. The oxide may also be prepared by the electrolysis of the fused pentoxide, or by the ignition of the oxychloride, $V_2O_2Cl_4 + 5H_2O$, in a current of carbonic acid gas:

$$V_2O_2Cl_4 + 5H_2O = V_2O_4 + 4HCl + 3H_2O.$$

Hypovanadic Hydroxide, $V_2O_4.7H_2O$ or $V_2O_2(OH)_4 + 5H_2O$, forms a greyish-white precipitate, obtained when a solution of hypovanadic sulphate or chloride is cautiously precipitated with a cold solution of sodium carbonate. When dried it is a black amorphous mass, having a glassy fracture. This on heating to 100° loses four molecules of water, leaving the hydrate $V_2O_4 + 3H_2O$. Hypovanadic oxide acts both as a basic and as an acid-forming oxide. When dissolved in acids the hypovanadic salts are formed,[1] whilst with alkalis the hypovanadates are produced.

The *hypovanadates* are all insoluble except those of the alkali metals, which are not derived from the normal hypovanadic acid, $H_4V_2O_6$, but from the partial anhydrides, $H_2V_2O_5$ and $H_2V_4O_9$. The alkali hypovanadates are obtained by adding an excess of caustic alkali to a concentrated solution of hypovanadic sulphate or chloride The dark-brown solution thus obtained with potash

[1] Guyard, *Bull. Soc. Chim.* 1876 [2], **25**, 350.

deposits *potassium hypovanadate*, $K_2V_4O_9+7H_2O$, in reddish-brown crystalline scales, which, after washing first with potash solution, and then with alcohol, may be dried between filter-paper. This salt is permanent in the air, and very soluble in water, yielding a dark-brown solution.

Sodium Hypovanadate, $Na_2V_4O_9+7H_2O$, is prepared in a similar way to the potassium salt, and exhibits analogous properties.

Ammonium Hypovanadate, $(NH_4)_2V_4O_9+3H_2O$, is obtained as a dark-brown crystalline precipitate by adding a hypovanadic sulphate solution to ammonia; it dissolves in water, yielding an almost black solution (Crow).

The hypovanadates of the heavy metals are insoluble precipitates.

Lead Hypovanadate, PbV_2O_5, is precipitated when a solution of lead acetate is added to a solution of potassium hypovanadate.

Silver Hypovanadate, $Ag_2V_2O_5$, is a black crystalline powder formed according to the following equation:

$$K_2V_4O_9+4AgNO_3+H_2O=2Ag_2V_2O_5+2KNO_3+2HNO_3.$$

Vanadium and Fluorine.

398 The oxides, V_2O_3, V_2O_4, and V_2O_5, all dissolve in hydrofluoric acid, but only the trifluoride, VF_3+3H_2O, has been isolated. A very large number of double salts of this fluoride and of the oxyfluorides VOF_2, VO_2F, and VOF_3 with hydrofluoric acid, metallic fluorides, and vanadium pentoxide has been described.[1] Only a few of the most characteristic are here mentioned.

Vanadium Trifluoride, VF_3+3H_2O, crystallises from the dark-green solution of vanadium trioxide in hydrofluoric acid, in dark-green readily soluble octohedra. The *double potassium salt*, $2KF.VF_3+H_2O$, is a bright green crystalline powder, which is precipitated when a solution of potassium fluoride is added to one of vanadium trifluoride.

Vanadium Oxydifluoride, VOF_2, is formed when the tetroxide is dissolved in hydrofluoric acid, and separates in blue prismatic crystals containing water. Several double salts with the fluo-

[1] Petersen, *J. pr. Chem.* 1889 [2], **40**, 193, 271. See also Piccini and Giorgiot, *Journ. Chem. Soc.* 1889, ii. 214; and Baker, *Journ. Chem. Soc.* 1878, i. 388.

rides of sodium, potassium, and ammonium may be prepared by adding solutions of these fluorides to the blue solution of the oxydifluoride (Petersen).

Vanadium pentafluoride, VF_5, is only known in the solution which is obtained by dissolving the pentoxide in hydrofluoric acid.

Potassium Vanadium Dioxyfluoride, $2KF.VO_2F$, is obtained by evaporating the pentafluoride solution almost to dryness, and adding it to potassium fluoride. It crystallises in golden-yellow six-sided prisms.

Vanadium pentoxide easily dissolves in a solution of hydrogen potassium fluoride with evolution of heat, and on cooling yellowish globular masses separate out, consisting of pearly, probably hexagonal, crystals, which have the composition $6KF.V_2O_5.2VOF_3+2H_2O$. The aqueous solution is yellow and possesses an acid reaction; the dry salt does not smell of hydrofluoric acid, and attacks glass only slowly. When this salt is dissolved in warm hydrofluoric acid, the compound $3KHF_2.2VOF_3$ is obtained in almost colourless tufts of needles, which when dry smell of hydrofluoric acid and attack glass (Baker).

Ammonium Fluoxyvanadates.—When the pentoxide is dissolved in ammonium fluoride no salt separates out on standing, but if more of the last-named salt be added, the compound $6NH_4F.V_2O_5.2VOF_3+2H_2O$, crystallises out in light-yellow, pearly, hexagonal scales. On solution in water and addition of more hydrogen ammonium fluoride, a fine yellow crystalline salt, $12NH_4F.V_2O_5.2VOF_3$, is precipitated in microscopic pyramids, and this dissolved in hydrofluoric acid, yields the compound $3NH_4HF_2.2VOF_3$, corresponding to one of the potassium salts. If sulphuretted hydrogen be passed into a solution of the pentoxide in hydrofluoric acid, the resulting blue solution evaporated and ammonium fluoride added to the concentrated liquid, transparent blue monosymmetric prisms of *ammonium fluoxyhyporanadate*, $2NH_4F.VOF_2+H_2O$, are deposited. *Zinc fluoxyvanadate*, $Zn_2OF_2.2VOF_3+14H_2O$, is formed by dissolving zinc carbonate and vanadium pentoxide in hydrofluoric acid. The salt crystallises in hard, yellow, monosymmetric prisms.

Vanadium and Chlorine.

399 The only compounds of vanadium and chlorine described before 1867 were oxychlorides. Three chlorides free from oxygen have been subsequently obtained either by the action

of chlorine on the nitride of vanadium, VN, or by distilling the oxychlorides over charcoal.[1] The following chlorides and oxychlorides of vanadium are now known :

CHLORIDES.

Vanadium tetrachloride .	VCl_4.
„ trichloride . .	VCl_3 or V_2Cl_6.
„ dichloride . .	VCl_2 or V_2Cl_4.

OXYCHLORIDES.

Vanadyl trichloride . .	$VOCl_3$.
„ dichloride . .	$VOCl_2$.
„ monochloride .	VOCl.
Divanadyl monochloride .	V_2O_2Cl.
Hypovanadic tetrachloride	$V_2O_2Cl_4+5H_2O$.
„ dichloride .	$V_2O_3Cl_2+4H_2O$.

Vanadium Tetrachloride, VCl_4, is formed when metallic vanadium or the mononitride is heated to redness in an excess of chlorine. It is best prepared by repeatedly passing the vapour of vanadium oxychloride, together with an excess of dry chlorine, over a long column of pure sugar-charcoal heated to a dull redness. Vanadium tetrachloride is a dark brownish-red thickish liquid, which evolves white fumes when exposed to moist air. It boils at 154° with partial decomposition, losing chlorine and leaving a residue of the sesquichloride. This decomposition also takes place at the ordinary temperature, especially on exposure to light. It does not solidify at −18°; its specific gravity at 0° is 1·8584, and the specific gravity of its vapour is 6·69, the calculated specific gravity being 6·675. When thrown into water the tetrachloride is at once decomposed, yielding a blue solution of hypovanadic chloride.

The tetrachloride heated in excess of chlorine splits up into trichloride and free chlorine, so that vanadium does not appear to form a penta-compound with chlorine.

Vanadium Trichloride, Vanadious Chloride, VCl_3.—The foregoing compound easily decomposes, as has been stated, into this body and chlorine. The trichloride is obtained either by the slow decomposition of the tetrachloride at the ordinary temperature or at its boiling-point, or, together with the dichloride

[1] Roscoe, *Phil. Trans.* 1869, 678.

when the vapour of the tetrachloride mixed with hydrogen is passed through a red-hot tube, as well as when the trisulphide is heated in chlorine.[1] It is a solid substance, crystallising in fine peach-blossom coloured, shining tables, closely resembling in appearance the crystals of chromium trichloride. It is non-volatile when heated in hydrogen, and decomposes when heated in the air, the pentoxide being formed. Ignited in a current of hydrogen, it first loses one atom of chlorine, forming the dichloride VCl_2, parting at a higher temperature with the whole of its chlorine, and leaving a residue of metallic vanadium as a lustrous grey powder. It is extremely hygroscopic, instantly deliquescing on exposure to moist air to a dark-brown liquid, which on addition of a drop of hydrochloric acid becomes green, forming a solution of vanadious chloride. The specific gravity of vanadium trichloride is 3·0; it readily dissolves in absolute alcohol and in ether, forming green-coloured solutions.

Vanadium Dichloride, Hypovanadious Chloride, VCl_2.—This is a solid body, crystallising in fine apple-green coloured plates, having a micaceous lustre and a hexagonal form. It is prepared by passing vanadium tetrachloride, mixed with dry and pure hydrogen, through a glass tube heated to dull redness. Its specific gravity at 18° is 3·23. It is very deliquescent, yielding a lavender-coloured solution of hypovanadious chloride, which possesses bleaching properties. When the dichloride is heated to whiteness in a current of dry ammonia, vanadium mononitride is obtained in bronze-coloured pseudomorphous crystals.

400 *Vanadium Oxychloride*, or *Vanadyl Trichloride*, $VOCl_3$. This compound, corresponding to phosphorus oxychloride, is obtained either by the action of chlorine on the oxides V_2O_2 and V_2O_3 as already described, or by heating a mixture of the pentoxide and charcoal in a current of chlorine:

$$V_2O_5 + 3C + 3Cl_2 = 2VOCl_3 + 3CO.$$

In the latter case the resulting liquid is red-coloured from the presence of tetrachloride, and is best purified by rectification over clean sodium in a current of carbon dioxide. Vanadyl trichloride thus obtained is a bright lemon-yellow coloured mobile liquid, boiling at 126°·7 and having a specific gravity at 14° of 1·841. It does not solidify at −15°. The specific gravity of its vapour is 6·108 at 186°, the calculated specific gravity being 6·003.

[1] Halberstadt, *Ber.* 1882, **15**, 1619.

On exposure to moist air vanadyl trichloride emits vapours of a cinnabar-red colour, and is soon decomposed in the presence of moisture into vanadic and hydrochloric acids. When a small quantity of water is added it becomes thick and blood-red coloured, owing to the formation of vanadic acid. A large quantity of water, however, yields a clear yellow solution. When the oxychloride is ignited in a current of dry ammonia gas, vanadium mononitride is obtained. Vanadium oxychloride combines with ether at 70°, forming a compound crystallising in long red needles and having the composition $VCl_3(OC_2H_5)_2$.[1]

When vanadium oxychloride is heated with zinc to 400°, vanadium dioxide and *vanadyl dichloride*, $VOCl_2$, are formed, the latter crystallises in green tables which deliquesce on exposure to moist air. The same compound is formed when the vapour of vanadyl trichloride and hydrogen are passed through a red-hot tube. In this case both *vanadyl monochloride* VOCl, and *divanadyl monochloride*, V_2O_2Cl, are likewise formed, the former as a flocculent brown powder insoluble in water, and the latter in the form of a yellow crystalline powder resembling mosaic gold. The molecular formula of these bodies is not known.

Hypovanadic Tetrachloride, $V_2O_2Cl_4+5H_2O$.—When vanadium pentoxide is dissolved in hot concentrated hydrochloric acid, chlorine is evolved, and a green solution is obtained, which becomes blue with deposition of sulphur when sulphuretted hydrogen is passed through the liquid. A brown amorphous deliquescent mass is obtained on evaporation, possessing the above composition. It dissolves in water, yielding a blue solution; but when treated with strong hydrochloric acid or alcohol the solution is brown, and this change is explained by the existence of two different hydrates.[2]

A compound of the formula $V_2O_3Cl_2+4H_2O$ has also been obtained as a dark green deliquescent mass, by the action of hydrochloric acid on vanadium pentoxide.[3]

Vanadium and Bromine and Iodine.

401 *Vanadium Tribromide*, VBr_3.—This is the only known compound of the above elements. It condenses as a greyish-

[1] Bedson, *Journ. Chem. Soc.* 1876, i. 309.
[2] Crow, *Journ. Chem. Soc.* 1876, i. 459.
[3] Ditte, *Compt. Rend.* 1886, **102**, 1310.

black compact amorphous sublimate, when dry bromine vapour is passed in excess over vanadium nitride, or over a mixture of vanadium trioxide and charcoal heated to redness. It is a very unstable compound, losing bromine even at the ordinary temperature in dry air, and deliquescing rapidly on exposure to moist air.

Vanadyl Tribromide, $VOBr_3$, obtained by passing dry bromine vapour over vanadium trioxide heated to redness, is a dark-red transparent liquid, having a density of 2·967 at 0°. It may be distilled under diminished pressure, passing over without decomposition, at a temperature of about 130° under a pressure of 100 m.m. When heated under the ordinary atmospheric pressure it suddenly solidifies at 180°, decomposing into *vanadyl dibromide*, $VOBr_2$, and free bromine. The latter oxybromide can be obtained directly by dissolving vanadium tetroxide in hydrobromic acid:

$$V_2O_4 + 4HBr = 2VOBr_2 + 2H_2O.$$

Hypovanadic Tetriodide, $V_2O_2I_4 + 8H_2O$, is formed by the action of hydriodic acid on vanadium pentoxide as a black deliquescent mass.[1]

Vanadium pentoxide also appears to form a double compound with iodine pentoxide.

Vanadium and Sulphur.

402 The sulphides of vanadium correspond to the oxides.[2]

Berzelius described a persulphide and a bisulphide of vanadium. Both of these, when prepared by precipitation according to the method given by him, seem to be mixtures of various oxysulphides. His bisulphide prepared in the dry way is in reality the trisulphide V_2S_3.

Vanadium Disulphide, V_2S_2, is formed when the trisulphide is strongly heated in a current of hydrogen. It forms a brownish-black powder or glistening brown scales, which dissolve slowly in dilute, but quickly in strong nitric acid. It dissolves slowly in alkali hydrosulphides yielding a violet solution.

Vanadium Trisulphide, V_2S_3.—This is the only vanadium salt free from oxygen prepared by Berzelius. He

[1] Ditte, *Compt. Rend.* 1886, **102**, 1310.

[2] Kay, *Journ. Chem. Soc.* 1880, i. 728.

obtained it by heating the trioxide in a current of suphuretted hydrogen. It can in like manner be prepared from the pentoxide, the oxychloride or any of the chlorides, but it is best obtained by acting on the ignited pentoxide with bisulphide of carbon vapour. It is a greenish-black powder possessing properties similar to those of the disulphide.

Vanadium Pentasulphide, V_2S_5, is formed by heating the foregoing with sulphur to 400°. It is a black powder which on heating in a current of carbon dioxide yields sulphur and the trioxide (Kay).

Ammonium Thiovanadate, $(NH_4)_3VS_4$, is obtained by passing sulphuretted hydrogen into a cooled solution of ammonium metavanadate in ammonia of specific gravity 0·898. The crystals resemble those of potassium permanganate. If weaker ammonia be employed, *ammonium hexasulphopyrovanadate*, $(NH_4)_4VS_6O$, is formed in dark-green crystals.

Hypovanadic Sulphate, $V_2O_2(SO_4)_2$, is deposited as a greenish-blue sandy powder by dissolving the tetroxide in excess of sulphuric acid and heating the solution for some time to the boiling-point of the acid.[1] If the tetroxide be dissolved in sulphuric acid, the solution evaporated, and the residue treated with absolute alcohol, a sky-blue powder remains, which deliquesces in moist air. If the solution be allowed to evaporate spontaneously over sulphuric acid, fine blue rhombic prisms having the composition $V_2O_2(SO_4)_2 + 4H_2O$ are deposited (Berzelius). An acid salt, $V_2O_2SO_4(SO_4H)_2+5H_2O$, is prepared by evaporating the sulphuric acid solution of the trioxide, drying the crystals on a porous plate, and then washing them with ether (Crow); and a similar salt, $V_2O_2SO_4(SO_4H)_2+3H_2O$, is obtained by precipitating a concentrated solution of any of the hypovanadic sulphates with concentrated sulphuric acid. Other hydrates and double salts of this series are also known; the composition of these compounds will be found in the memoirs above referred to.

Normal Vanadyl Sulphate, $(VO)_2(SO_4)_3$, is obtained, according to Berzelius, by dissolving the pentoxide in hot sulphuric acid which has been diluted with half its weight of water.[2] On evaporating at a low temperature the salt crystallises out in reddish-brown, very deliquescent scales. The same compound is obtained in ruby-red octohedra by boiling the pentoxide with

[1] Gerland, *Ber.* 1877, **10**, 2109.

[2] See also Ditte, *Compt. Rend.* 1886, **102**, 757.

an excess of sulphuric acid. When these are heated to the melting-point of lead, the basic salt $(VO)_2O(SO_4)_2$ remains as a red mass exhibiting small bright crystalline faces.

If the pentoxide be dissolved in concentrated sulphuric acid and the solution evaporated, the basic salt $VO(OH)SO_4$ is formed[1] as a sandy reddish-yellow powder. According to Gerland this is identical with the preceding compound.

When potassium vanadate is dissolved in strong sulphuric acid and the excess of acid driven off by heat, the double salt $K_2SO_4 + (VO)_2(SO_4)_3$ is obtained as a yellow crystalline powder (Berzelius).

Vanadium Alums.—Several alums have been prepared by treating a metavanadate with sulphurous acid in the presence of sulphuric acid and then reducing electrolytically. *Ammonium vanadium alum*, $(NH_4)_2SO_4 + V_2(SO_4)_3 + 24H_2O$, crystallises in hemihedral forms of the regular system, and is violet. Alums containing potassium, rubidium, caesium, and thallium have also been prepared.[2]

Vananadium and Nitrogen, Phosphorus and Arsenic.

403 *Vanadium Mononitride*, VN.—The process described by Berzelius for preparing metallic vanadium by heating the ammonio-oxychloride in an atmosphere of ammonia does not yield the metal, but the mononitride, vanadium being distinguished from most other metals by its power of direct union with nitrogen. The substance obtained by strongly igniting the ammonio-oxychloride in a current of dry ammonia (or rather of its component gases) at a white-heat is a greyish-brown powder, which does not undergo change at ordinary temperatures. The mononitride is likewise obtained when the black residue left on calcining ammonium metavanadate in the air is heated to whiteness in a current of dry ammonia. Another and still more simple plan of obtaining the nitride is to expose the oxide to the action of ammonia gas at a white-heat. It is a singular fact that in the presence of nitrogen and hydrogen the whole of the oxygen should be replaced by nitrogen.

When heated in the air vanadium mononitride glows and slowly oxidises to the blue oxide.

[1] Gerland, *Ber.* 1878, **11**, 98.

[2] Piccini, *Zeit. Anorg. Chem.* 1896, **11**, 106; *Chem. Centr.* 1897, i. 223.

Vanadium Dinitride, VN_2, is obtained as a black powder by passing ammonia over vanadyl trichloride, heating the residue in a glass tube to expel sal-ammoniac, washing with water, and drying in a vacuum over sulphuric acid.

404 Extended series of phosphovanadic and arsenovanadic acids and their derivatives have been described by Berzelius,[1] Ditte,[2] and Gibbs.[3] According to Friedheim [4] these substances are phosphates and arsenates of vanadium (and double salts of these with the vanadates), in which vanadic oxide acts as a weak base. They can be prepared by bringing the requisite salts together.

Vanadic Phosphate, $2VO_2.PO(OH)_2 + 9H_2O,(P_2O_5.V_2O_5 + 11H_2O)$, is formed when vanadic oxide is heated with syrupy phosphoric acid, and crystallises in golden-yellow flakes.

Vanadic Arsenate, $V_2O_5.As_2O_5 + 10H_2O$, is prepared in a similar manner, and forms yellow crystals.

Vanadium and Carbon.

Vanadium Carbide, VC, is formed when vanadic anhydride is heated with carbon in the electric furnace. It forms hard crystals of the specific gravity 5·36, burns in oxygen, and becomes incandescent when heated in chlorine.[5]

Detection and Estimation of Vanadium.

405 Insoluble vanadium compounds can be brought into solution either by treatment with acids or with alkalis. The hydrochloric acid solution assumes a bright blue colour on the addition of zinc. A solution of hypovanadic sulphate cannot be distinguished in colour from one of copper sulphate when diluted to the requisite extent with water. It however, of course, does not become colourless in presence of metallic iron. Solutions of certain vanadates also closely resemble solutions of the chromates. Thus, for instance, a solution of the tetravanadate of potassium does not differ in appearance from one of potassium

[1] *Lehrbuch*, (6), **3**, 1037.
[2] *Compt. Rend.* 1886, **102**, 757.
[3] *Amer. Chem. Journ.* 1885-6, **7**, 118, 209.
[4] *Ber.* 1890, **23**, 1530, 2600.
[5] Moissan, *Compt. Rend.* 1896, **122**, 1297.

dichromate. They may, however, be distinguished from one another, inasmuch as the vanadate solution becomes blue, whilst the chromate assumes a green colour on deoxidation. When a solution of vanadic acid or an acid solution of an alkali vanadate is shaken up with ether containing hydrogen peroxide, the aqueous solution assumes a red colour like that of ferric acetate. This reaction serves to detect 1 part of vanadic acid in 40,000 parts of the liquid. Chromic acid does not interfere with the reaction.[1]

For the *quantitative* determination of vanadium, von Hauer proposed the precipitation of ammonium metavanadate, insoluble in solution of sal-ammoniac. This on ignition yields the pure pentoxide. But this separation of vanadic acid from the metals of the alkalis by means of chloride of ammonium gives too low results, both as regards the vanadium and the alkali. It is almost impossible to prevent traces of ammonium metavanadate from dissolving, and on ignition, even with the greatest care, some portions of the finely-divided vanadium pentoxide are invariably carried off when the ammonia escapes. On the other hand, the volatilisation of the comparatively large quantities of sal-ammoniac which must be employed in order to ensure the complete precipitation of the vanadium almost always entails a considerable loss of the fixed alkali chlorides. A far more accurate plan for the separation of vanadium is the precipitation of the soluble vanadate by acetate of lead, when basic lead vanadate is precipitated, which is so insoluble that a portion when finely powdered and boiled in water does not dissolve in sufficient quantity to enable the lead to be detected in the filtrate by the reaction with sulphuretted hydrogen. The salt is also insoluble in acetic acid, but it dissolves readily in nitric acid, liberating vanadic acid, which separates out, but dissolves completely when the liquid is warmed. In the analysis of a soluble vanadate this insoluble lead salt is collected on a filter dried at 100° and weighed; a given quantity of the dried salt is then dissolved in nitric acid, the lead precipitated by pure sulphuric acid, and the lead sulphate determined with the usual precautions by evaporation, addition of alcohol, &c. The lead sulphate thus obtained is (contrary to Berzelius's statement) quite free from vanadium, whilst the vanadium pentoxide in the filtrate is obtained perfectly pure and well crystallised on evaporation and ignition. The filtrate from the lead vanadate,

[1] G. Werther, *J. pr. Chem.* 1863, **88**, 195.

freed from excess of lead by means of sulphuric acid and evaporated, yields the alkali sulphate, not containing a trace of vanadium. Vanadium may be very readily determined volumetrically when no other reducible metals are present. For this purpose the solution of vanadic acid in sulphuric acid is diluted and reduced to tetroxide by passing a current of sulphur dioxide through it and afterwards boiling to expel the excess of this gas. Standard permanganate is then added until a permanent coloration is obtained.

406 The *atomic weight* of vanadium has been determined in two ways. The first is by igniting vanadium pentoxide in dry hydrogen, when it is reduced to the trioxide, and the atomic weight of vanadium is then deduced by the relation,

$$\frac{a}{b}=\frac{2x+5\times 15{\cdot}88}{2x+3\times 15{\cdot}88}, \text{ whence } x=7{\cdot}94\,\frac{(5b-3a)}{a-b}$$

where a is the weight of vanadium pentoxide taken, and b is the weight of trioxide obtained.

The following results were obtained by Roscoe:[1]

	Weight of pentoxide taken.	Weight of trioxide obtained.	Atomic weight of vanadium.
(1) . .	7·7397	6·3827	50·97
(2) . .	6·5819	5·4296	51·00
(3) . .	5·1895	4·2819	51·09
(4) . .	5·0450	4·1614	50·96

The mean atomic weight of these four experiments is 50·98, with a mean error of 0·065. Berzelius found as a mean of four experiments that 120·927 parts of pentoxide yielded 100 of the trioxide; which gives, according to the above equation, $x=52{\cdot}06$ This difference is probably due to the fact that the vanadium employed by Berzelius contained a trace of phosphorus, which prevented the complete reduction.

The second method for the determination of the atomic weight was the analysis of vanadyl trichloride. The chlorine in this compound was estimated both by Gay-Lussac's volumetric process and by gravimetric analysis. Nine volumetric determinations gave 61·306 per cent. of chlorine, and eight gravimetric analyses gave 61·241 per cent. of chlorine, the atomic weight from the mean of the seventeen determinations being 50·90. The mean atomic weight of vanadium, according to both methods, is 50·94 (O = 15·88).

[1] *Phil. Trans.* 1868, 6.

NIOBIUM, Nb 93·5.

407 This metal is so closely connected with the next one, tantalum, that it will be most convenient to consider their history together.

In the year 1801, Hatchett[1] laid before the Royal Society an investigation on a mineral from Massachusetts, which he believed to contain a new metal, to which he gave the name of *columbium*. In the following year, Ekeberg,[2] in Sweden, investigating the yttrium minerials, discovered a new element in a mineral to which he afterwards gave the name of yttrotantalite, whilst the same element also occurred in a mineral termed tantalite. In consequence of this he named the metal *tantalum*, partly because mythological names were frequently used, and partly also as pointing to the fact "that when placed in the midst of acids it is incapable of taking any of them up and saturating itself with them."

In 1809, Wollaston[3] endeavoured to show that columbium and tantalum were identical, and a few years later Berzelius[4] more carefully investigated the oxides of the last-named metal obtained from tantalite, and prepared tantalic acid. Afterwards, in 1839, Wöhler[5] found that the acid forming oxide contained in pyrochlor and in the Bavarian tantalites possessed peculiar properties; and Rose[6] then observed that the columbites of Bodenmais contained the oxide of a new metal, to which he gave the name of niobium, and in 1846 he thought that he had found a third new metal, to which he gave the name of *pelopium*. In 1853 he came to the conclusion on further investigation that niobic acid and pelopic acid were different oxides of niobium, and to the first of these he gave the name of niobic acid, whilst the latter was designated as hyponiobic acid. These, however, exhibited "a relationship so peculiar that the whole range of chemistry does not furnish an example of a similar kind."[7] In 1856-7, Hermann observed that niobium and tantalum usually occur together, whilst in 1864-5, Blom-

[1] *Phil. Trans.* 1802, 49.
[2] *Ann. de Chim.* **43**, 276.
[3] *Phil. Trans.* 1809, 246.
[4] *Pogg. Ann.* **4**, 6.
[5] *Pogg. Ann.* 1839, **48**, 91.
[6] *Pogg. Ann.* 1844, **63**, 307, 693; 1846, **69**, 118.
[7] *Pogg. Ann.* 1853, **90**, 471.

strand[1] showed that Rose's hyponiobic chloride contains oxygen, and is an oxychloride, and Marignac[2] almost at the same time proved that the double salts which hyponiobic fluoride forms with metallic fluorides, are isomorphous with similar double salts containing titanium fluoride, TiF_4, and tungsten oxyfluoride, WO_2F_2. Inasmuch as the sum of the atoms in all these isomorphous compounds is constant, and as, according to analysis, the hyponiobic fluoride contains three atoms of fluorine for one of oxygen, Marignac concluded that it must be an oxyfluoride of the composition, $NbOF_3$, and he succeeded in obtaining experimental evidence of the truth of this view. At the same time he showed that tantalic acid, which up to that time had been supposed to be analogous to titanic acid, and to which the formula TaO_2 had been given, must, like the highest oxide of niobium, be a pentoxide, as these two oxides occur in isomorphous mixture in several minerals, and as both metals form isomorphous double fluorides, such as K_2TaF_7 and K_2NbF_7.

The truth of this view of the composition of the niobium and tantalum compounds was confirmed by the experiments of Deville and Troost,[3] who in 1865 determined the vapour densities of niobium chloride, niobium oxychloride, and tantalum chloride, which were found to correspond to the formulæ $NbCl_5$, $NbOCl_3$, and $TaCl_5$. The investigations of Blomstrand and Marignac next showed that the metal *dianium*, supposed by v. Kobell to be contained in various columbites, is in fact identical with niobium, and Marignac further showed that *ilmenium*, which Hermann believed he had discovered in samarskite, is a mixture of niobium and tantalum. It appears certain that *neptunium*, also discovered by Hermann, is a similar mixture. In the United States of America the name columbium is patriotically retained for niobium.

408 Niobium and tantalum are found in many other minerals in addition to those already mentioned. The following table gives the composition of some of the more important of these.

[1] *J. pr. Chem.* 1866, **97**, 37.
[2] *Ann. Chim. Phys.* 1866, [4], **8**, 5, 49.
[3] *Compt. Rend.* 1865, **60**, 1221.

Tantalite (*analysed by Rammelsberg*).

Locality	Finland.	Sweden.
Ta_2O_5	76·34	49·64
Nb_2O_5	7·54	29·27
SnO_2	0·70	2·49
FeO	13·90	13·77
MnO	1·42	2·88
	99·90	98·05

Columbite (*analysed by Blomstrand*).

Locality . . .	Greenland.	Massachusetts.	Bodenmais.
Ta_2O_5 . . .	—	28·55	22·79
Nb_2O_5 . . .	77·97	51·53	56·43
WO_3 . . .	0·13	0·76	1·07
SnO_2	0·73	0·34	0·58
FeO	17·33	13·54	15·82
MnO . . .	3·28	4·55	2·39
ZrO_2 . . .	0·13	0·34	0·28
MgO . . .	0·23	0·42	0·40
PbO	0·12	—	—
H_2O	—	0·16	0·35
	99·92	100·19	100·11

Pyrochlor (*analysed by Rammelsberg*).

Locality . . .	Siberia.	Kaiserstuhl.
Nb_2O_5	53·19	47·13
TiO_2	10·47	13·52
ThO_2	7·56	—
Ce_2O_3	7·00	7·30
CaO	14·21	15·94
MgO	0·22	0·19
FeO	1·84	10·03
Na_2O	3·71	3·12
F	3·06	2·90
	101·26	100·13

Yttrotantalite, Fergusonite, Euxenite (*analysed by Rammelsberg*).

	Yttrotantalite.	Fergusonite.	Euxenite.
Locality . .	Ytterby.	Greenland.	Arendal.
Ta_2O_5 . .	10·05	6·30	—
Nb_2O_5 . .	42·12	44·45	35·83 ?
WO_3 . . .	0·22	0·15	—
SnO_2 . . .	0·24	0·47	24·33
Y_2O_3 . . .	27·69	24·87	17·23
Er_2O_3 . .	12·44	9·81	9·39
Ce_2O_3 . .	1·90	2·00	2·34
CaO . . .	3·21	0·61	—
FeO . . .	0·63	0·74	3·61
UO_2 . . .	1·26	2·58	8·86
La_2O_3 . .	—	5·63	—
H_2O . . .	—	1·49	—
	99·76	99·10	101·59

Besides occurring in these minerals, niobium and tantalum are frequently found in small quantities in tinstone, wolfram, pitchblende, and other minerals.

For the purpose of preparing the niobium and tantalum compounds, tantalite, fergusonite, or some other mineral containing these metals, is finely powdered and fused with three times its weight of acid potassium sulphate, the fused mass completely boiled out with water, and the residue digested with sulphide of ammonium, in order to remove tin and tungsten, the iron present being at the same time converted into sulphide. The residue is washed and boiled with dilute hydrochloric acid, when the hydroxides of niobium and tantalum, together with titanic acid and silica, remain behind, and are then well washed with boiling water. The mass is dissolved in hydrofluoric acid, filtered from any residue, and heated to remove silicon fluoride. Titanium, niobium, and tantalum are then separated by the different solubilities of their double potassium fluorides. To the boiling hydrofluoric acid solution 1 part of potassium fluoride is added for every 4 parts of oxide present, and the solution concentrated until 1 gram of oxide is contained in 7 cc. of the solution. On cooling, fine needle-shaped crystals of potassium tantalofluoride separate out, mixed with titanofluoride. These are washed with water until the wash-water after standing for two hours does not give an orange-red precipitate, but a sulphur-yellow one with tincture of galls. On evaporating the mother-liquor and the wash-water, more of the salt is obtained, which at last is mixed with scales of the niobium salt. The potassium tantalofluoride purified by recrystallisation is then mixed with its own weight of concentrated sulphuric acid and heated gradually to 400°, and the residue boiled out with water, when a granular crystalline compound of tantalum oxide and sulphuric acid remains behind. This is decomposed by ignition, and it is advisable to add ammonium carbonate in order to get rid of the whole of the sulphuric acid.

The filtrate from the tantalum salt deposits the compound $2KF, NbOF_3.H_2O$, when it is concentrated, and from this the niobic oxide may be prepared by decomposition with sulphuric acid and washing or continued boiling with water. The double fluoride thus obtained is not always pure, but may be purified by repeatedly boiling with water, and reconverting the white deposit, which has the formula $2KF, 3NbO_2F$, into the normal

oxyfluoride by treatment with hydrofluoric acid and potassium fluoride.[1]

The minerals may also be brought into solution by fusion with acid potassium fluoride, this process being specially suitable for columbite. (Gibbs.)

409 The metal was first obtained by Blomstrand,[2] by reducing the chloride in hydrogen, as a mirror-like deposit on the tube, but it was not certain whether this was the pure metal or a hydride. Roscoe[3] obtained it in the form of a steel-grey crust, by passing the vapour of the pure chloride together with hydrogen repeatedly through a red-hot tube; this was then more strongly heated in a porcelain tube, through which hydrogen was passed. The metal contained only 0·27 per cent. of hydrogen as well as a small quantity of chloride and oxide, the latter being derived from diffused air. At 15°·5 it has a specific gravity of 7·06. It takes fire at a low temperature when heated in the air, oxidising with vivid incandescence, and also burns in chlorine when slightly warmed. It is hardly attacked by hydrochloric or nitric acid or aqua-regia even when heated, but dissolves in concentrated sulphuric acid, yielding a colourless liquid.

When the double fluoride with potassium is heated with sodium and the product treated with water, a mass is obtained which has a metallic appearance, but contains about 1 per cent. of hydrogen corresponding in composition with the formula NbH (Marignac). It resembles the metal in its behaviour to acids, and like this burns when heated in the air.[4]

COMPOUNDS OF NIOBIUM.

Niobium and Oxygen.

410 *Niobium Dioxide*, NbO or Nb_2O_2, is formed when dry potassium niobium oxyfluoride is heated with sodium under a layer of potassium chloride over a gas blow-pipe and was thought by Rose to be the metal. The fused mass is boiled with water,

[1] Krüss and Nilson, *Ber.* 1887, **20**, 1676.
[2] *J. pr. Chem.* 1866, **97**, 37.
[3] *Mem. Manch. Lit. and Phil. Soc.* [3], 6, 186.
[4] Krüss and Nilson, *Ber.* 1887, **20**, 1691.

and the residue washed with water and afterwards with dilute alcohol. It then forms a white powder which on heating in the air oxidises with vivid incandescence. When gently warmed in chlorine gas it burns with formation of oxychloride, and it dissolves in the moist state in hydrochloric acid with evolution of hydrogen. If the vapour of the oxychloride be passed over heated magnesium wire, the same compound is formed in crystals which probably belong to the regular system.

Niobium Tetroxide, NbO_2 or Nb_2O_4, is obtained as a heavy black powder, which appears blue by reflected light, by heating the pentoxide very strongly in hydrogen. This oxide is also formed when niobic oxide is heated with metallic magnesium.[1] It is not attacked by acids and burns in the air when heated to redness.

Niobium Pentoxide, Nb_2O_5 is best prepared from Greenland columbite which, as already mentioned, is converted into potassium nioboxyfluoride; this is purified by repeated crystallisation, and then decomposed with sulphuric acid and the solution boiled with water. It is a white amorphous infusible powder having a specific gravity of 4·53, and becomes crystalline when strongly heated. It may be obtained in prismatic crystals by fusion with boron trioxide or borax.

Niobium Hydroxide or *Niobic Acid*, $HNbO_3$, is formed by the decomposition of the oxychloride or pentachloride in moist air or by water. It is a white powder which, when dried at 100°, retains varying quantities of water, and is converted with incandescence into the pentoxide at a red heat. It is only slightly soluble in hot hydrochloric acid, but the residue, after this treatment, can be dissolved in water. On the addition of zinc the solution becomes blue and a hydrated precipitate, probably of Nb_2O_4, separates out. The solution of niobic acid obtained by treatment with hydrochloric acid gives on the other hand a brown colour with zinc, and a brown oxide separates out which has the composition $Nb_3O_5(NbO + 2NbO_2)$. Niobic acid is easily soluble in caustic alkalis and their carbonates.

411 *Potassium Hexaniobate*, $K_8Nb_6O_{19}+16H_2O$, is prepared by fusing the pentoxide with double its weight of potassium carbonate, dissolving in water, and evaporating in a vacuum. It forms large glistening monosymmetric crystals which effloresce on exposure to air. If caustic potash be added to this solution and the mixture slowly evaporated, fine rhombic pyramids of

[1] Smith and Maas, *Zeit. anorg.* 1894, **7**, 96.

$K_6Nb_4O_{13}+13H_2O$ are deposited, and these effloresce quickly on exposure.[1]

When equal molecules of niobium pentoxide and potassium carbonate are fused together, a distinctly crystalline mass is obtained, which, when treated with water, yields the salt $2K_2Nb_4O_{11}+11H_2O$. If, however, a larger quantity of potassium carbonate be employed, the compound $K_4Nb_2O_7+11H_2O$ is obtained.[2]

The crystallised sodium niobates described by Rose were prepared from a mixture of the oxides of niobium and tantalum. According to Marignac, these crystallise indistinctly, and appear to be mixtures. The niobates of the metals of the other groups have been prepared by Joly, and correspond closely to the tantalates.

Numerous crystalline niobates have been prepared by fusing the precipitated salts with the corresponding chlorides or with boric acid.[3]

Niobium and the Halogens.

412 *Niobium Pentafluoride*, NbF_5.—This substance, like the fluoride of tantalum, is only known in solution, and possesses analogous properties to the latter compound.

Niobium Oxyfluoride, $NbOF_3$, is obtained by igniting a mixture of pentoxide and fluor-spar in a current of hydrochloric acid, in the form of small crystals, closely resembling zirconium fluoride. It forms double salts with other metallic fluorides, of which those of potassium and ammonium have been investigated by Marignac, who has prepared the following:

$(KF)_2NbOF_3+H_2O$.	$(NH_4F)_2NbOF_3$.
$(KF)_3NbOF_3$.	$(NH_4F)_3NbOF_3$.
$(KF)_5(NbOF_3)_3+H_2O$.	$(NH_4F)_5(NbOF_3)_3+H_2O$.
$(KF)_4(NbOF_3)_3+2H_2O$.	NH_4FNbOF_3.
$HF(KF)_3NbOF_3$.	$(NH_4F)_3NbOF_3NbF_5$.

These are crystallisable, and are formed by dissolving niobic acid in a larger or smaller quantity of hydrofluoric acid, and adding the other fluorides in various proportions. The first salts of the two series, which Marignac terms normal salts, are

[1] Marignac, *Ann. Chim. Phys.* 1866, [4], **8**, 20.
[2] Santesson, *Bull. Soc. Chim.* 1875 [2], **24**, 53.
[3] Lanson, *Zeit. anorg. Chem.* 1896, **12**, 188.

those which are readily formed. The normal potassium salt is formed whenever the others are recrystallised, and is deposited in the form of thin monosymmetric scales isomorphous with potassium tungsten oxyfluoride, $(KF)_2WO_2F_2$, and with potassium titanofluoride, K_2TiF_6. By dissolving this in hot hydrofluoric acid *potassium niobofluoride*, K_2NbF_7, is formed, which is deposited in glistening rhombic needles. The normal ammonium salt crystallises in rhombic tablets, and is isomorphous with ammonium tungsten oxyfluoride, $(NH_4F)_2WO_2F_2$.

A double fluoride of the formula $2KF,3NbO_2F$, is deposited in small quantity as a white powder when a solution of the normal potassium oxyfluoride is boiled for some time. [1]

$$3(2KF.NbOF_3)+3H_2O=2KF,3NbO_2F+4KF+6HF.$$

It is readily soluble in hydrofluoric acid.

413 *Niobium Trichloride*, $NbCl_3$, is obtained when the vapour of the pentachloride is slowly passed through a red-hot glass tube, and when the oxide is heated with phosphorus pentachloride.[2] It either forms crystalline crusts which have the appearance of iodine, or is found crystallised in long needles which are dichroic. It is neither volatile nor deliquescent, and is not decomposed by water or ammonia, but is easily oxidised by nitric acid. When heated in the air it emits thick vapours, and when ignited in a current of carbon dioxide it forms niobium oxychloride, $NbOCl_3$, and carbon monoxide, a reaction which is not exhibited by any other metallic chloride (Roscoe).

Niobium Pentachloride, $NbCl_5$.—When an intimate mixture of niobium pentoxide and a large excess of sugar charcoal is heated in a current of chlorine perfectly free from air, yellow needles of the above compound are formed. These fuse at 194°, and boil at 240°·5, but begin to sublime at 125°. The yellow vapour has a specific gravity of 9·6 (Deville and Troost), the formula requiring 9·38. It dissolves in hydrochloric acid, forming a liquid, which gelatinises on standing, and when diluted with water or on boiling almost all the niobic acid separates out. Metallic zinc brought into the solution turns it a deep blue colour.

Niobium Oxychloride, or *Niobyl Chloride*, $NbOCl_3$, is formed by the direct union of the dioxide with chlorine, and also when a mixture of pentoxide with a small quantity of carbon is heated

[1] Krüss and Nilson, *Ber.* 1887, **20**, 1676.
[2] Pennington, *Chem. News*, 1897, **75**, 38.

in chlorine. It is likewise formed by repeatedly distilling the pentachloride in a current of carbon dioxide over ignited pentoxide. It is a colourless fibrous crystalline mass, which volatilises without melting at about 400°, giving rise to a colourless vapour, of which the specific gravity was determined by Deville and Troost to be 7·88, theory requiring 7·48. When heated in carbon dioxide, and still more readily in hydrogen, it decomposes into pentoxide and pentachloride. It deliquesces on exposure to moist air, with formation of crystallised niobic acid, whilst when brought into contact with water it decomposes violently, forming amorphous niobic acid.

When niobium oxide is heated in hydrogen chloride a hydroxychloride, $Nb_2O_4,3H_2O,HCl$ is formed which is volatile at a high temperature.[1] Hydrogen bromide yields an analogous compound.

Niobium Pentabromide, $NbBr_5$, is prepared in the same way as the chloride, and is a purple-red mass, which on heating becomes yellow and volatilises.

Niobium Oxybromide, $NbOBr_3$.—When a mixture of pentoxide and double its weight of carbon is heated in bromine vapour a yellow voluminous mass is obtained, which sublimes without fusion, and when heated in carbon dioxide is converted into the pentoxide.

Niobium and Sulphur.

414 *Niobium Oxysulphide*, $NbOS_3$ is formed when carbon dioxide mixed with the vapour of bisulphide of carbon is passed over the white-hot pentoxide. It is a black or brass-coloured crystalline powder. The same compound is easily obtained, as a black woolly mass, by heating the oxychloride in sulphuretted hydrogen. This powder, when rubbed in an agate mortar, attains a steely lustre, and when heated burns in the air with formation of pentoxide.

Niobium and Nitrogen.

415 When niobium pentoxide is heated to whiteness in ammonia, it loses the half of its oxygen, and forms a black powder containing nitrogen. If niobium oxychloride be treated with dry ammonia, it becomes hot and turns yellow. This, when heated

[1] Smith and Maas, *Zeit. anorg. Chem.* 1894, **7**, 96.

gives off sal-ammoniac, and a black powder remains behind, which, when melted with caustic potash, yields ammonia in large quantity, and on heating in the air burns with incandescence. It is not attacked either by boiling nitric acid or aqua-regia, but dissolves readily in a mixture of hydrofluoric and nitric acids.

Detection and Estimation of Niobium.

416 The solution of a niobate yields with potassium ferrocyanide and hydrochloric acid a deep brown precipitate. Under some circumstances tincture of galls or tannic acid gives an orange-red precipitate. When zinc is added to the acidified solution the whole becomes blue and afterwards brown. In the presence of potassium thiocyanate, zinc and hydrochlorci acid produce a bright golden brown coloration. Microcosmic salt or borax easily dissolves the pentoxide, and a bead is obtained which becomes violet, blue, or brown, in the reducing flame and red on the addition of ferric oxide.

The *quantitative* determination and separation of niobium is best understood from the following description of Rose's method, given by Rammelsberg, for the analysis of tantalites and columbites.[1] The mixture of oxides obtained by fusion with acid potassium sulphate and lixiviation with water, is fused with sulphur and sodium carbonate, and the fused mass treated with water, when any tin sulphide or tungsten sulphide which may be present is dissolved. The residual oxides of tantalum and niobium are then treated with dilute sulphuric acid in order to remove the iron, and again fused with acid potassium sulphate, and the oxides separated out by boiling the mass with water, whilst any iron, manganese, zinc, copper, or tin which may still be present is found in solution.

In order to separate niobium from tantalum the purified oxides are fused with potassium fluoride, the mass digested with a large quantity of water, and the solution boiled after addition of some hydrofluoric acid. On cooling, the largest portion of the tantalum separates out chiefly as tantalofluoride. The filtrate is evaporated to two-thirds its bulk, allowed to stand twenty-four hours in the cold, and the rest of the salt thus obtained. Sometimes a third evaporation of the filtrate is necessary. The

[1] *Pogg. Ann.* 1872, **146**, 56.

potassium tantalofluoride can then be weighed, but it generally contains some iron which must be separated by heating with sulphuric acid, the purified tantalum being weighed as the pentoxide.

The solution which contains the niobium is also evaporated with sulphuric acid, the residue ignited and well washed with water, and again ignited, when niobium pentoxide remains behind. This may still contain a trace of titanium. In order to free it from this metal the fluo-double-salts are warmed with hydrochloric acid and zinc, when the titanium compound is reduced, and its amount estimated by volumetric analysis with potassium permanganate.

The *atomic weight* of niobium was determined by Marignac[1] to be 93·5, from numerous analyses of potassium niobium oxyfluoride and niobium pentachloride.

TANTALUM, Ta, 181.

417 Pure tantalum does not appear to have been prepared. Probably that got by Berzelius was the purest form that has yet been seen. This he obtained by igniting potassium fluotantalate with potassium. It is a black powder which assumes an iron-grey metallic lustre under the burnisher, and when gently heated takes fire in the air and burns to oxide. It dissolves in hydrofluoric acid with evolution of hydrogen, but in no other acids, not even in aqua-regia. Heated gently in chlorine, it burns brightly, and it also takes fire when heated in sulphur vapour.

COMPOUNDS OF TANTALUM.

Tantalum and Oxygen.

418 *Tantalum Tetroxide*, Ta_2O_4, is formed when the pentoxide is heated in a very small carbon crucible, exposed to the highest heat of a wind furnace or with metallic magnesium. It is a porous dark-grey mass which scratches glass, and when rubbed on a hone has a steel-grey colour. It gives a dark brown non-metallic powder, and is not attacked by acids even by a mixture

[1] *Ann. Chim. Phys.* 1866 [4], 8, 16.

of hydrofluoric and nitric acids, but burns when heated with formation of the pentoxide.

Tantalum Pentoxide, Ta_2O_5. The preparation of this body has already been described. It is a white amorphous infusible powder which when strongly heated becomes crystalline, and when ignited with boron trioxide or melted with microcosmic salt in a porcelain furnace is obtained in rhombic prisms. When gently heated it has a specific gravity of 7·35, which after exposure to a white heat rises to 8·01. It does not dissolve in any acid, but volatilises completely when ignited with ammonium fluoride.

Tantalum Hydroxide or Tantalic Acid, $HTaO_3$, is obtained in the form of a gelatinous mass, when the chloride is quickly mixed with water. If, however, the same compound be exposed to moist air until it is decomposed, and then mixed with water containing ammonia, the hydroxide is obtained as a crystalline powder, which when dried at 100° possesses the above composition, and is converted, with vivid incandescence, into pentoxide when heated to low redness. The hydroxide obtained by ignition with acid potassium sulphate does not exhibit this phenomenon. Tantalic acid dissolves in binoxalate of potash, in hydrofluoric acid, and, when freshly precipitated, in other acids.

The Tantalates.

419 The normal tantalates, to which class the tantalum minerals belong, are all insoluble in water. Besides these, others are known, derived from the unknown hydrate, hexatantalic acid, $H_8Ta_6O_{19}$, of which only the compounds of the alkali-metals are soluble in water.

Potassium Hexatantalate, $K_8Ta_6O_{19}+16H_2O$, is formed by dissolving the acid in caustic potash, and also by fusing the pentoxide with double its weight of caustic potash. The fused mass is dissolved in water and allowed to evaporate in a vacuum. Transparent glistening monosymmetric crystals are thus obtained which dissolve in lukewarm water without decomposition. On boiling or evaporating in the air salts containing more tantalum are formed. If it is repeatedly ignited with sal-ammoniac and washed with water the normal salt, $KTaO_3$, is obtained.

Sodium Hexatantalate, $Na_8Ta_6O_{19}+25H_2O$, is obtained in a similar way to the potassium salt, a vivid incandescence occurring

when the mixture is heated to redness. The fused mass is treated with water, the residue dissolved in hot water, and either allowed to cool or, inasmuch as it is insoluble in caustic soda, poured on to the top of a strong solution of this substance. It crystallises in small hexagonal tables which dissolve at 13°·5 in 493, and at 100° in 162 parts of water. It is not decomposed by boiling water, and if the aqueous solution is mixed with alcohol, a precipitate of $NaTaO_3+H_2O$ is formed, and this becomes anhydrous on ignition. The anhydrous salt is also formed by the ignition of the hexatantalate.

Ammonium Tritantalate is produced by the addition of sal-ammoniac to a solution of the sodium salt, and is a precipitate which resembles chloride of silver, and is slightly soluble in water. Its composition is uncertain.

When tantalum pentoxide is strongly ignited with the chlorides of calcium, magnesium and other metals, crystalline tantalates of these metals are obtained.[1]

Tantalum and the Halogens.

420 *Tantalum Pentafluoride*, TaF_5, is only known in solution. If this be evaporated even at a moderate temperature, some of the fluorine volatilises whilst tantalic acid remains behind. Tantalum fluoride forms double salts with the other metallic fluorides.

Potassium Tantalofluoride, K_2TaF_7. The mode of preparing this salt has been already described. It forms small rhombic needles which readily melt, but it does not decompose when ignited even to whiteness in a platinum vessel. It is easily soluble in hot, though sparingly so in cold water. When the solution is boiled for some time decomposition takes place, a white powder of the oxyfluoride, $K_4Ta_4O_5F_{14}=4KF+2TaF_5+Ta_2O_5$, separating out. This reaction serves to detect the smallest quantity of tantalum when present together with niobium oxyfluoride (Marignac).

Sodium Tantalofluoride, $Na_2TaF_7+H_2O$, is obtained in a similar manner to the potassium salt, or by dissolving sodium hexatantalate in hydrofluoric acid. On evaporation indistinct crystals of Na_3TaF_8, separate out, and then eight-sided rhombic tables of the above salt, which lose their water under 100°.

[1] Joly, *Compt. Rend.* 1875, **81**, 266 and 1266.

Ammonium Tantalofluoride, $(NH_4)_2TaF_7$. This is produced when ammonia is added to a hydrofluoric acid solution of tantalic acid until a precipitate begins to form, the solution then being evaporated. It crystallises in thin quadratic scales or needles which are easily soluble in water.

When tantalic acid is dissolved in an acid solution of ammonium fluoride, regular octohedra are obtained on evaporation which have the composition, $3NH_4F + TaOF_3$.

Tantalum Chloride, $TaCl_5$, is obtained by heating an intimate mixture of the pentoxide and carbon in a current of chlorine, and is also formed when the pentoxide is heated with phosphorus pentachloride. It forms light yellow needles and prisms which melt at 211° and boil at 242°, but begin to volatilise at so low a temperature as 144°, and may be readily sublimed in a current of carbon dioxide or chlorine. The specific gravity of the vapour, according to Deville and Troost, is 12·8, the calculated density being 12·42. It fumes in the air, and is converted into tantalic acid.

Tantalum Pentabromide, $TaBr_5$, is prepared in a similar way to the chloride, and in its properties closely resembles this compound.

Tantalum and iodine do not combine.

Tantalum and Sulphur.

421 *Tantalum Tetrasulphide*, Ta_2S_4, is obtained by acting upon white hot tantalum pentoxide, with a mixture of hydrogen and the vapour of carbon bisulphide. It is a grey finely-granular friable mass, which may be pressed into masses resembling graphite, and these on burnishing possess the colour of brass. It is also formed when the chloride is ignited in a stream of sulphuretted hydrogen, and is thus obtained in crusts resembling pyrites in appearance. It is not attacked by hydrochloric acid even on boiling, and nitric acid and aqua-regia oxidise it but slowly.

Tantalum and Nitrogen.

422 When tantalum chloride is heated in ammonia gas to a temperature not above the point of volatilisation of the sal-ammoniac which is formed, an amorphous yellowish-red mass of Ta_3N_5 is obtained. If the temperature then be raised to redness

black tantalum nitride, TaN, is obtained, and this exhibits a metallic lustre when burnished. H. Rose, who first obtained this compound, believed it to be the metal.

Detection and Estimation of Tantalum.

423 In order to detect tantalum in a mineral, tantalic acid must be prepared from it, and this converted into a soluble tantalate. If ferrocyanide of potassium be added to this solution, a characteristic yellow precipitate falls down, and under the same circumstances tincture of galls likewise produces a bright yellow precipitate. The tantalum compounds do not colour a bead of borax or of microcosmic salt.

Tantalum is determined quantitatively either as the pentoxide or as potassium tantalofluoride, the process having been described under niobium. The *atomic weight* was determined by Marignac,[1] who analysed the potassium and ammonium tantalofluorides and obtained the number 181 (O = 15·88).

ANTIMONY (STIBIUM) Sb = 119·4.

424 This metal occurs in nature chiefly as stibnite, antimonite or antimony sulphide, Sb_2S_3, a mineral which was known in very early times, having been long employed, as indeed is yet the case, by women in the East for painting the eyebrows. In St. Jerome's translation of the Hebrew of Ezekiel xxiii. 40, we read "circumlinisti stibio oculos tuos;" and in the Second Book of Kings ix. 30 we find, "Porro Jezebel introitu eius audito depixit oculos suos stibio." Of this latter passage Cheyne and Driver give as the translation of the Hebrew "set her eyes in paint (literally antimony)."

The name for this mineral in Hebrew and Arabic is "Kohl," and this word passed as "alcool" or "alkohol" into other languages; thus in the Spanish translation of the Bible the above passage from Ezekiel is thus rendered, "Alcoholaste tus ojos." In the middle ages the word alcohol served to designate any fine powder, and it was only at a later period that it was employed to mean spirits of wine. Dioscorides calls this metal *στίμμι*, and mentions that it is also known by other terms, such

[1] *Ann. Chim. Phys.* 1866 [4], **9**, 251.

as πλατυόφθαλμον, the eye-expander, γυναικείον, belonging to womankind, &c. Pliny, on the other hand, terms it *stibium*. The Latin Geber, who also was acquainted with this substance, termed it *antimonium*, and up to the time of Lavoisier both these words were made use of to signify sulphide of antimony. The German name for this substance was *spiessglas*, which was afterwards changed to *spiessglanz*. As already mentioned (vol. i. 8), the works attributed to "Basil Valentine," which have hitherto been regarded as the earliest known records concerning antimony and its derivatives, have been shown by the late Prof. Schorlemmer to be forgeries dating from about 1600. There is no doubt, however, that the iatro-chemists, from the time of Paracelsus, were acquainted with many antimonial preparations, and numerous references to these are scattered throughout the chemical literature of the times. The statements of "Basil Valentine" may still serve to show the condition of knowledge concerning antimony in 1600. He makes the following remarks as to the name of the sulphide in his *Triumphal Car of Antimony*: "In order, as is most proper, that I may say something about the name of the material, it should be understood that this material was long known to the Arabians, and from ancient time was termed by them *asinat*. The Chaldeans entitled it *stibium*, and in the Latin tongue it has been called *antimonium*[1] up to the latest times, and in our own German mother tongue the same material has been foolishly called spiessglas for this reason, that this material can be fluxed and a glass made from it."

Dioscorides mentions that in order to roast the crude antimony it must be heated in a current of air until it burns, for if more strongly ignited, it melts like lead. This passage has given rise to the supposition that the author was acquainted with metallic antimony, and that this is probably the case is shown by the fact that an old Chaldean vase analysed by Berthelot consisted of pure antimony.[2] Antimony was confounded with bismuth by some chemists, such as Libavius, even so late as the sixteenth century.

The preparation of the metal was described by "Basil Valentine" who in his *Wiederholung des Grossen Steins der*

[1] The story of the accidental poisoning of certain monks by spiessglas having given rise to the name of the metal (antimoine) is on the face of it improbable, and must, as Kopp remarks, have been invented by a Frenchman, whereas Valentine wrote in German!

[2] *Compt. Rend.* 1887, **104**, 265.

uralten Weisen terms it *spiessglas rex* and also *plumbum antimonii.* It has already been stated that the alchemists considered that each semi-metal was simply a variation of a true metal.

425 Antimony occurs in many other minerals besides stibnite. The metal is found, though not frequently, in the native state, and also as arseniferous antimony or allemontite, As_3Sb. Antimony also occurs as the trisulphide, Sb_2S_3, combined with basic sulphides, and in these thioantimonites a portion of the antimony is usually replaced by arsenic. Amongst such compounds are berthierite, $FeS.Sb_2S_3$; wolfsbergite or antimonial copper, $Cu_2S.Sb_2S_3$; boulangerite, $3PbS.Sb_2S_3$; jamesonite, $2PbS.Sb_2S_3$; bournonite $(Cu_2,Pb)_3Sb_2S_6$; pyrargyrite or red silver ore, $3Ag_2S.Sb_2S_3$, &c. In addition to these we have dyscrasite or antimonial silver, Ag_3Sb; breithauptite or antimonial nickel NiSb; ullmannite or nickeliferous grey antimony, NiSbS; valentinite or antimony oxide, Sb_2O_3; cervantite or antimony ochre, Sb_2O_4, and stiblite, $Sb_2O_4+H_2O$. Antimony is also found in small quantity in iron ores, ferruginous waters, in the coal formation, and in river sand.

426 *Preparation of Metallic Antimony.* The preparation of the metal from the sulphide is a very simple operation. In order to free the ore from quartz or other earthy admixture, the mineral is either melted in vertical cylinders which have a hole at the bottom out of which the molten sulphide drops, or the preliminary fusion is carried on in reverberatory furnaces. The purified sulphide is then either fused with metallic iron, or is roasted in order to convert it into the oxide, and this is reduced with carbon or with crude tartar. "Basil Valentine" describes both of these methods in his account of the preparation of the philosopher's stone; he states: "Antimonium is a master in medicine, and from it by means of cream of tartar and salt a King (regulus) is made, steel-iron being added to the spiessglas during fusion. Thus by an artifice a wonderful star is obtained which the learned before my time have termed the philosophical signet star." In the *Triumphal Car of Antimony* he gives the following receipt: "Take good Hungarian spiessglas and with the same quantity of crude tartar, and half as much saltpetre rub these small and let them fuse well in a wind furnace; afterwards pour out into a mould and allow to cool when a regulus is found."

In order to reduce the oxide obtained by roasting the ore, it is mixed either with 20 per cent. of powdered charcoal which

has been saturated with concentrated soda, or with 10 per cent of crude tartar, and the mixture of ore and reducing agent melted in a large earthen crucible. In this country three operations are necessary for the production of the best star-antimony. The first of these is termed "singling"; in this 40 parts of the sulphide are mixed with about 20 parts of thin scrap iron, and this is then melted in plumbago crucibles, when metallic antimony and iron sulphide are formed. The fusion lasts about an hour and a half, and when complete the charge is poured into conical moulds. The crude metal is then separated from the slag, consisting chiefly of sulphide of iron, which floats on the surface, and it is again melted in the second process of "doubling," with an addition of a small quantity of sodium sulphate and slag obtained in the following operation. The charge for each pot is 80 lbs. of crude antimony, 2 lbs. of salt-cake and 2 lbs. of slag, and the fusion lasts about an hour and a quarter. The metal is cast in moulds, allowed to cool, and broken into small pieces ready for the third process, termed "melting for star-metal." For this purpose 2 parts of pearl-ash and 5 parts of slag from a previous operation of the same kind are added to 60 parts of metal and the fusion again repeated. The molten metal is then poured into square moulds in which it is allowed to cool slowly, the surface being at the same time completely covered with slag in order that it may attain the peculiar crystalline structure which is required in commerce. Most of the antimony of commerce is reduced in England, foreign ores, especially those from Borneo, being employed.

It has been already stated that "Basil Valentine" was acquainted with the crystalline surface exhibited by pure antimony, but he specially mentions that the regulus which is not starred possesses exactly the same composition as that which presents this peculiarity. He, as well as some of his contemporaries, believed that the stellated surface was only produced when iron was employed in the preparation, whilst other chemists taught that the preparation of the stellated antimony did not depend on the presence of iron, but was connected with a favourable conjunction of the stars. Indeed this latter opinion was pretty generally held until the time of Boyle, who however entirely discredits this explanation, and also states that the starred metal can be obtained without the use of iron.

In his essay *On the Unsuccessfulness of Experiments*, Boyle [1]

[1] *Opera*, ed. 1772, **1**, 325.

says: "And it may perhaps also be from some diversity either in antimonies or irons, that eminent chemists have (as we have observed) often failed in their endeavours to make the starry regulus of *Mars* and antimony. Insomuch that divers artists fondly believe and teach (what our experience will not permit us to allow) that there is a certain respect to times and constellations requisite to the producing of this (I confess admirable) body. Upon this subject I must not omit to tell you that a while since an industrious acquaintance of ours was working on an antimony, which unawares to him, was, as we then supposed, of so peculiar a nature, that making a regulus of it alone without iron, the common way (for his manner of operation I inquired of him), he found, to his wonder, and showed me his regulus adorned with a more conspicuous star than I have seen in several stellate reguluses of both antimony and *Mars*."

Lemery, in his *Cours de Chymie*, published in 1675, also argues strongly against the supposition that the planet Mars has anything to do with the formation of the stellated surface.

Commercial antimony often contains traces of silver, gold, arsenic, iron, lead, copper, and frequently some sulphur. In order to prepare the pure metal Liebig's process is the best; this consists in fusing 16 parts of the metal with 2 parts of sodium carbonate, and 1 part of sulphide of antimony for an hour; on cooling the regulus is separated from the slag, and melted again for an hour with 1½ part of sodium carbonate, and this operation again repeated with 1 part of this salt.[1] According to Schiel[2] a small quantity of nitre should be added from time to time. By means of this repeated fusion the whole of the arsenic is separated, provided that a sufficient quantity of iron be originally present in the metal; should this not be the case, it is necessary to add about 2 per cent. of iron sulphide.[3]

Another method of purifying the metal is that described by Wöhler, and improved by Meyer,[4] and this is available when the only impurity present is arsenic. In this process, one part of the metal is ignited with 1·25 parts of sodium nitrate, and 0·5 part of sodium carbonate. The pulverised mass is dissolved in water when pure sodium metantimonate remains behind; this is then reduced by heating with half its weight of cream of tartar or with a mixture of carbon and sodium carbonate.

427 *Properties.*—Antimony is a lustrous silver-white metal,

[1] *Annalen*, 1857, **104**, 223.
[2] *Annalen*, 1835, **19**, 22.
[3] Bensch, *Annalen*, 1847, **63**, 273.
[4] *Annalen*, 1848, **66**, 238.

which when slowly cooled exhibits a coarsely laminated crystalline fracture. When quickly cooled, on the other hand, the fracture is granular. It crystallises in obtuse rhombohedra which can scarcely be distinguished from cubes, and has a specific gravity of 6·71 to 6·86. Native antimony occurs in scaly masses, usually containing silver, iron, and arsenic. Its most important localities are at Sahl in Sweden, Andreasberg in the Harz, Przibram in Bohemia, in the Dauphiny, in Canada, the United States, Mexico, Chili, Sarawak in Borneo and Queensland. Native antimony has a specific gravity of from 6·5 to 7.

Antimony is hard, and so brittle that it can be powdered; it melts at 629·5°,[1] and volatilises at a bright red-heat in the air, or in a current of a gas, but not when fused under a layer of common salt. It may be distilled in a current of hydrogen at a white-heat. The vapour density of antimony is 10·743 at 1572° and 9·781 at 1640° (Meyer and Biltz),[2] numbers which are intermediate between those required for the molecular formulæ Sb_2 and Sb. It does not undergo any alteration on exposure to the air at the ordinary temperature; on heating it burns to form the oxide, and when heated on charcoal before the blowpipe, the oxide is evolved in thick white fumes, and a portion of it is deposited as a white incrustation on the charcoal. If the blast of air be stopped the globule of molten metal begins to glow and is seen to be covered with a crystalline network of needles of oxide, and when the globule is thrown from some height on to a piece of paper, the edges of which are turned up, it breaks into many smaller globules which burn with a very bright flame. Cold water as well as dilute sulphuric acid does not act upon the metal at the ordinary temperature, but at a red-heat it decomposes steam with formation of oxide. Nitric acid converts it into a white powder, the composition of which depends on the strength of the acid, nitrogen peroxide being evolved and no ammonia formed.[3] Pure antimony does not dissolve in strong hydrochloric acid in the absence of oxygen,[4] but the ordinary metal is easily dissolved by hot hydrochloric acid as well as by cold aqua regia, and when heated with concentrated sulphuric acid is converted into antimony sulphate. Antimony combines directly with the elements of the chlorine group, with those of the sulphur group and with phosphorus and arsenic.

[1] Heycock and Neville, *Journ. Chem. Soc.* 1895, **1**, 186.
[2] *Ber.* 1889, **22**, 725. See also *Annalen*, 1887, **240**, 317.
[3] Montemartini, *Journ. Chem. Soc.* 1892, ii. 1402.
[4] Ditte and Metzner, *Compt. Rend.* 1892, **115**, 936.

428 *Explosive or Electrolytic Antimony.* This peculiar substance, discovered by Gore,[1] is formed by the union, under certain conditions, of antimony and antimony trichloride. It is obtained by electrolysis of an acid solution of antimony trichloride, having a specific gravity of 1·35, or of a solution obtained by dissolving the trioxide in from 5 to 6 times its weight of hydrochloric acid of specific gravity 1·12, metallic antimony being, in each case, used as the positive, and copper or platinum as the negative pole. The latter becomes covered with a grey lustrous metallic coating, having an amorphous fracture and a specific gravity of 5·78. It contains from 4·8 to 7·9 per cent. of antimony chloride, together with a small quantity of free hydrochloric acid. When scratched with a metallic point or touched with a red-hot wire it decomposes with evolution of heat and liberation of the chloride, and when heated to 200° it flies into powder with a loud explosion. If it be preserved under cold water it does not undergo any alteration, but when heated to 75° it decomposes with a hissing sound; hydrochloric acid is found in solution, and the water becomes turbid owing to the formation of basic antimony chloride. Similar products are obtained by the electrolysis of acid solutions of the bromide and iodide (Gore).

Uses.—Antimony is employed for the preparation of tartar emetic, and of other products used in pharmacy and in many processes of calico printing and dyeing. Its alloys are also largely used in the arts. When antimony is precipitated by zinc from a solution of the trichloride, the metal is obtained in a finely pulverulent state, as *antimony black*; this is employed for the purpose of imparting to the surface of gypsum figures and other objects the appearance of iron or steel.

Antimony Alloys.

429 "Basil Valentine" mentions that antimony is valuable for the preparation of medicines, and that it is likewise employed for other purposes, such as for the preparation of printer's type. He adds that under certain favourable conjunctions of the planets alloys are made of antimony, and from these seals and amulets are cast, which are said to possess special virtues. These same alloys can, according to Valentine, be cast in the same way to form both bells and mirrors.

[1] *Phil. Trans.* 1858, 185; 1859, 797; 1862, 323; Pfeifer, *Annalen*, 1881, **209**, 61.

English type-metal is an alloy of lead, antimony, and tin. A small percentage of copper is sometimes added, but is found of little practical value.

The value of antimony in these alloys is that it imparts to them hardness, and gives them the property of expanding in the act of solidification so necessary in order to obtain an accurate cast of the letter. The tin gives toughness and coherence to the metal. The following are analyses of English type-metal;[1] No. I. is a specially tough metal:

	I.	II.	III.	IV.
Lead . .	50	55·0	61·3	69·2
Antimony.	25	22·7	18·8	19·5
Tin . . .	25	22·1	20·2	9·1
Copper .	—	—	—	1·7

German type-metal contains about 15 per cent. of antimony.

Britannia-metal and *Pewter*. This silver-white metal is largely used for the preparation of spoons, cups, and other articles. It consists mainly of tin and antimony, but frequently contains other metals, as is shown by the following analyses:

	Britannia Metal.		Plate Pewter.	Ashbury Metal.	Métal Argentin.
Tin . . .	85·7	81·9	89·3	77·8	85·5
Antimony .	10·4	16·2	7·1	19·4	14·5
Copper . .	1·0	—	1·8	—	—
Zinc . . .	2·9	1·9	—	2·8	—
Bismuth .	—	—	1·8	—	—

White- or *anti-friction metal* is chiefly used for lining the brasses of various parts of locomotive engines, and for the solid bushes for the coupling-rods. Several alloys are used for this purpose, as is seen by the following analyses:

	I.	II.	III.
Copper	5·3	1·5	5·0
Antimony . . .	10·5	13·0	10·0
Tin	84·2	45·5	85·0
Lead.	—	40·0	—
	100·0	100·0	100·0

[1] Varrentrapp, *Dingl. Polyt. Journ.* 1865, **175**, 38.

No. I. is a metal used at the Crewe works; No. II. is one known as Babbit's metal; and No. III. one used by the German locomotive makers.

The alloy employed for the manufacture of ships' nails consists of 3 parts of tin, 2 of lead, and 1 of antimony.

Brass articles can be covered with a fine lustrous coating of antimony by dipping them into a hot solution of 1 part of tartar emetic, 1 of tartaric acid, and 3 of water, to which 3 or 4 parts of hydrochloric acid and as much powdered antimony have been added. The peculiar crystallographic relations of these alloys have been already referred to (p. 70).

Antimony forms a beautiful purple alloy with copper which has the composition Cu_2Sb, and is known as Regulus of Venus.

COMPOUNDS OF ANTIMONY.

Antimony and Hydrogen.

430 *Antimony Hydride*, or *Stibine*, SbH_3. This substance was first prepared in 1837 by Lewis Thompson,[1] and also, independently, by Pfaff[2] and other chemists. It is formed when nascent hydrogen is brought into contact with a soluble antimony compound, or when an alloy of potassium or sodium with antimony is decomposed by water, or an alloy of zinc and antimony by dilute hydrochloric or sulphuric acid. It is also formed when antimony oxide is added to an acid solution which is evolving hydrogen. All these methods, however, furnish a gas which is largely mixed with free hydrogen. According to F. Jones,[3] a relatively pure gas is obtained by allowing a concentrated solution of antimony in strong hydrochloric acid to drop slowly on to an excess of granulated or pulverized zinc. The gas thus obtained quickly undergoes partial decomposition, so that the interior of the evolution-flask becomes covered with a mirror-like coating of antimony, and the evolved gas contains at most 4 per cent. of antimony hydride. Like arsine the gas is formed from its elements with absorption of heat, the heat of formation being about $-84{,}500$ c.[4] Stibine

[1] *Phil. Mag.* 1837 [3], **10**, 353. [2] *Pogg. Ann.* 1837, **41**, 339.
[3] *Journ. Chem. Soc.* 1876, i. 641.
[4] Berthelot and Petit, *Compt. Rend.* 1889, **108**, 546.

possesses a most disagreeable smell and taste. Water at 10° dissolves from 4 to 5 volumes, and fish die in a few hours in water thus saturated, but they recover if, when still alive, they are thrown into fresh water. Antimony hydride is easily inflammable, burning with a greyish flame and evolving white fumes of antimony oxide. When the gas is passed through a glass tube heated above 150° metallic antimony is deposited close to the heated spot in the form of a lustrous mirror, and if this be heated more strongly, small metallic globules are seen by the microscope to have been formed. Concentrated sulphuric acid decomposes the gas. Caustic alkali solution becomes deep brown when the gas is passed through it, and at last a black powder separates out. The brown solution absorbs oxygen rapidly, and especially if it be shaken with air. The brown powder thus obtained appears to possess the composition $Sb(OH)_3$. It rapidly decomposes on standing, becoming richer in antimony. When antimony hydride is passed through a solution of silver nitrate, black silver antimonide, $SbAg_3$, is deposited, mixed with metallic silver arising from the action of free hydrogen upon the silver salt. Sulphur decomposes the gas in sunlight or on heating to 100°, but not in the dark, and becomes itself covered with a film of the orange-red antimony sulphide (F. Jones):

$$2\ SbH_3 + 6S = Sb_2S_3 + 3H_2S.$$

Sulphuretted hydrogen acts in the same way even in the dark:

$$2SbH_3 + 3H_2S = Sb_2S_3 + 6H_2.$$

Antimony and Oxygen.

431 Considerable doubt formerly existed as to the number of the oxides formed by antimony. Thénard, in 1800, mentions several; whilst Proust, in 1804, admitted the existence of only two. The exact number was ascertained by Berzelius in 1812 to be as follows:

Antimony trioxide, Sb_4O_6.
Antimony tetroxide, Sb_2O_4.
Antimony pentoxide, Sb_2O_5.

All these are acid-forming oxides; the first acting also as a feebly basic oxide.

Antimony Trioxide, Sb_4O_6. This occurs as the mineral valentinite, with other ores of antimony, having been produced by the oxidation of these. It forms pearly-white rhombic crystals which are sometimes coloured yellow or red by the presence of iron and other metals, and have a specific gravity of 5·566. Another, though less frequent form of antimony trioxide, is senarmontite, which usually occurs together with other antimony ores, and crystallises in regular octohedra, having a specific gravity of 5·2 to 5·3. From this it appears that antimony trioxide is isodimorphous with arsenious oxide. Both these crystalline forms can be artificially prepared. Thus when the metal or sulphide is heated in an inclined crucible a light white oxide is formed at a red-heat, and this, when more strongly heated, is deposited on the upper part of the crucible in glistening needles, sometimes mixed with octohedra, and known as *flores antimonii*, or flowers of antimony. This latter form is also observed when the rhombic oxide is sublimed, and the octohedra, when quickly heated, are converted into the rhombic crystals.[1] Both forms are also obtained by crystallising a hot saturated solution of the oxide or chloride in sodium carbonate (Mitscherlich). Antimony trioxide is prepared by diluting an acid solution of the oxide with water, and washing the basic salts which are thrown down, first with hot water, then with sodium carbonate solution, again with water, and finally converting the residue into oxide by ignition. Obtained in this way, the oxide is a pale buff-coloured crystalline powder, which can also be obtained, but not perfectly pure, by oxidising the metal with very dilute nitric acid. It is scarcely soluble in water, and becomes yellow when ignited, but assumes the pale buff tint again on cooling.

At a dark red-heat it melts, and the mass obtained on cooling is crystalline. It volatilises at 1560°, yielding a vapour having a specific gravity of 19·9 corresponding to the molecular formula Sb_4O_6.[2] It is insoluble in dilute sulphuric acid and in nitric acid, but is easily soluble in hydrochloric and tartaric acids, and the caustic alkalis. The solution of antimony trioxide in cream of tartar yields *potassium antimonyl tartrate* or *tartar emetic*, $C_4H_4KSbO_7$. Heated in the air it absorbs oxygen, the tetroxide[3] being formed at all temperatures between 390–775°;

[1] Terreil, *Compt. Rend.* 1866, **62**, 302.
[2] V. and C. Meyer, *Ber.* 1879, **12**, 1282.
[3] Carnelley and Walker, *Journ. Chem. Soc.* 1887, i. 86.

at very high temperatures however, the latter decomposes and the trioxide is again formed.[1] The trioxide is readily reduced when it is heated in hydrogen. According to Bunsen the presence of higher oxides can be easily detected by the addition of potassium iodide to the hydrochloric acid solution, when iodine is set free, as may be readily ascertained by shaking the liquid with a few drops of carbon bisulphide.

The trioxide in solution is readily converted into antimonic acid by means of oxidising agents such as iodine, chlorine, or potassium dichromate. The change cannot be completely effected by bromine water, nitric acid or potassium chlorate and hydrochloric acid.[2]

The mineral valentinite was probably known to the ancients. Pliny states that two kinds of stibium exist: "*Duo ejus genera mas et femina. Horridior est mas scabriorque et minus ponderosus, minusque radians et arsenosior; femina contra nitet, friabilis, fissurisque, non globis, dehiscens.*" Perhaps, however, under the feminine variety he may have understood the preparation obtained by roasting the sulphide, for this process is mentioned by Dioscorides, and Glauber also refers to it. The operation is more fully described by "Basil Valentine." He says: "From the common regulus of the spiessglas magnificently fine *flores* may be prepared both yellow, red, and white," by regulating the fire carefully. Valentine certainly knew that the mineral which we now call valentinite is an ore of antimony, for he distinguishes between the black- and the golden-spiessglas. The oxide obtained by roasting the metal reduced by iron was formerly called *nixferrum*, as it was believed that iron was necessary for its formation.

Antimony trioxide acts as a weak acid-forming oxide and also as a weak basic oxide. The salts formed by the action of strong acids are decomposed by water with formation of basic salts, which in contact with water are gradually converted into the oxide.

432 *Antimonious acid.* Two hydrates of antimony trioxide have been described, which may be considered as the ortho- and pyro-acids, although it is not certain that they are definite compounds, since the amount of water contained in them varies gradually with the temperature at which they are dried. The hydrate corresponding to the meta-acid $HSbO_2$ has not been

[1] Read, *Journ. Chem. Soc.* 1894, i. 314.
[2] Bošek, *Journ. Chem. Soc.* 1895, i. 515.

obtained. The ortho-acid, H_3SbO_3, is obtained by adding nitric acid to antimonyl tartaric acid or tartar emetic and drying the precipitate at 100°. The pyro-acid, $H_4Sb_2O_5$, is formed by adding copper sulphate to a solution of antimony sulphide in caustic potash until no further orange-coloured precipitate is thrown down, but a white precipitate is formed. After filtration the liquid, on addition of acetic acid, yields a precipitate having the above composition.[1]

Only sodium and potassium salts have as yet been obtained in the crystalline condition, and these appear to be salts of the (unknown) meta-acid $HSbO_2$.

Sodium Antimonite, $NaSbO_2+3H_2O$, separates out from a hot solution of the oxide in caustic soda in glistening octohedra, which are difficultly soluble in water.

Hydrogen Sodium Antimonite, $NaSbO_2+2HSbO_2$, is obtained from very concentrated solutions in large crystals almost insoluble in water, which, like those of the former compound, appear to belong to the monosymmetric system.[2]

Potassium Triantimonite, $K_2O,3Sb_2O_3$ is formed in crystals when the trioxide is boiled with caustic potash.[3]

Antimony Tetroxide or *Antimonious-Antimonic Oxide*, Sb_2O_4. By some chemists this substance is considered to be a compound of the trioxide and pentoxide of antimony (Sb_4O_8). It is a white powder formed when either of the two other oxides is strongly heated in the air. When heated it becomes temporarily yellow, and dissolves only with difficulty in acids. Antimony-ash, obtained by roasting the sulphide in the air, is an impure tetroxide, and was formerly employed for the preparation of the antimony compounds. Impure tetroxide also occurs as the mineral cervantite, found together with other antimony ores in Tuscany. Antimony tetroxide forms salts with basic oxides which have been termed *hypoantimonates*.

Potassium Hypoantimonate, $K_2Sb_2O_5$, is obtained by fusing together the tetroxide and potash, and lixiviating the fused mass with cold water. It is a white mass which is soluble in hot water; on addition of hydrochloric acid to this solution the acid salt $K_2Sb_4O_9$ separates out.

Other insoluble hypoantimonates can be obtained by double decomposition with the corresponding salts. Some of these

[1] Schaffner, *Annalen*, 1844, **51**, 182.
[2] Terreil, *Ann. Chim. Phys.* 1866 [4], **7**, 380.
[3] Cormimbœuf, *Compt. Rend.* 1892, **115**, 1305.

occur as minerals. Thus romeite, $CaSb_2O_5$, crystallises in quadratic pyramids, and is found at St. Marcel, in Piedmont; and ammiolite, which occurs as a powder coloured red by the presence of cinnabar, found in Chili, is probably a copper hypoantimonate, $CuSb_2O_5$.

Antimony Pentoxide and the Antimonic Acids.

433 *Antimony Pentoxide*, Sb_2O_5, is obtained by rapidly evaporating the powdered metal or its lower oxides with nitric acid, and gently heating the residue. This product usually contains a small amount of the lower oxides, but the pure oxide may be prepared by gently heating the precipitate produced by adding dilute nitric acid to a solution of potassium antimonate. It is a light yellow powder, having a specific gravity of 5·6, practically insoluble in water, and turning blue litmus-paper red. Nitric acid does not dissolve it, whilst concentrated hydrochloric acid only attacks it slowly, but at last dissolves it completely; it volatilises completely when heated with sal-ammoniac. It is reduced to the trioxide when it is heated with hydriodic acid or treated with stannous chloride solution. Antimony pentoxide acts as a stronger acid forming oxide than the trioxide, and at the same time as a weaker base, the only stable salts being the sulphide, fluoride and chloride, all of which have the typical formula SbR'_5.

Antimonic Acid.—Antimony pentoxide is said to form several distinct hydrates, which correspond in composition to the hydrates of phosphorus pentoxide and are known by similar names. A certain amount of confusion exists in the nomenclature of these acids since Berzelius gave the name of antimonic acid to the hydrate, $HSbO_3$, the true metantimonic acid, whereas the true pyroantimonic acid, $H_4Sb_2O_7$, was termed metantimonic acid by Frémy, and the same system extended to the salts.

The composition of all the acids which have been described depends on the temperature at which they have been dried, and it is very doubtful whether they are really definite hydrates.

The *ortho-acid*, H_3SbO_4, is formed when potassium antimonate is decomposed by dilute nitric acid and the precipitate dried at 100°. The *meta-acid*, $HSbO_3$, is formed when this is heated to 175°. These substances are white powders which are soluble

in aqueous potash, slightly soluble in water, and are converted into the pentoxide when heated. The meta-acid was formerly known under the name of *materia perlata*, and was employed as a medicine.

The *pyro-acid*, $H_4Sb_2O_7$ (Frémy's metantimonic acid), is formed by the decomposition of the pentachloride by hot water. The air-dried precipitate possesses the formula $H_4Sb_2O_7 + 2H_2O$,[1] and has the same composition as volgerite, a mineral which occurs in the province of Constantine, in Algeria. When dried at 100° it becomes anhydrous, and it dissolves rather more readily in water than antimonic acid, and is also soluble in cold ammonia. When heated to 200°, or when kept under water, it is converted into metantimonic acid.

434 *The Antimonates.*—Since the time of Berzelius, the antimonates have been chiefly investigated by Frémy [2] and Heffter,[3] Beilstein and Bläse,[4] Knorre and Olschewsky,[5] and Ebel.[6]

Considerable doubt still exists as to the constitution of these compounds, since most of them contain water, and it is doubtful whether this belongs to the constitution of the salt or is water of crystallisation.

Potassium Antimonate, $KSbO_3$, is obtained by deflagrating one part of metallic antimony with four parts of saltpetre and lixiviating with warm water. A white powder is thus obtained, which when boiled for some time with water dissolves to a considerable extent. On concentrating the solution to a certain point, a crystalline mass separates, but if the liquid be further evaporated, a gum-like mass, $2KSbO_3 + nH_2O$, is obtained which dissolves readily in warm water. When dried at 100°, this salt contains $3H_2O$, and at 185° still contains $2H_2O$. When a current of carbonic acid gas is passed through a solution of the normal salt, a sparingly soluble acid salt is precipitated which has the formula $2K_2O.3Sb_2O_5 + 7H_2O$ at 100°, and still contains $2H_2O$ at 350°. This salt was probably known to the iatro-chemists, and was much employed by quack doctors and known as *antimonium diaphoreticum ablutum*. The substance obtained by deflagrating the sulphide with saltpetre was employed at the end of the 17th century under the name *antimonium*

[1] Daubrawa, *Liebig's Ann.* 1877, **186**, 110.
[2] *Ann. Chim. Phys.* 1844, [3], **12**, 499, and 1848, **23**, 407.
[3] *Pogg. Ann.* 1852, **86**, 418.
[4] *Journ. Chem. Soc.* 1889, ii. 1123.
[5] *Ber.* 1887, **20**, 3043.
[6] *Ber.* 1889, **22**, 3044.

diaphoreticum non ablutum, and Libavius and others treated this residue with acids in order to obtain their diaphoreticum, which, therefore, consisted chiefly of antimonic acid.

Normal Potassium Pyroantimonate, $K_4Sb_2O_7$, was described by Frémy (under the name of metantimonate), but the substance obtained by him was probably a mixture of caustic potash and potassium antimonate. A sparingly soluble *acid salt*, $K_2H_2Sb_2O_7 + 7H_2O$, can however be prepared by oxidising an alkaline solution of potassium antimonite with potassium permanganate and evaporating the filtrate (Knorre and Olschewsky).[1]

Sodium Antimonate, $2NaSbO_3 + 7H_2O$, is obtained when the metal or sulphide is deflagrated with Chili saltpetre and the mass washed out with water. At 200° it loses two molecules of water, but it does not become anhydrous until it attains a red-heat.

A salt which is probably identical with this is formed as a voluminous white precipitate, when sodium chloride is added to a solution of the gummy potassium antimonate. This changes on standing into the crystalline *acid sodium pyroantimonate*, $H_2Na_2Sb_2O_7 + 6H_2O$. This salt is only soluble in 350 parts of cold water and is the least soluble of the salts of sodium. A solution of potassium antimonate can therefore be used as a reagent for the detection of sodium. Even when a solution contains only 0·1 per cent of sodium salt, a crystalline powder separates out after standing for twelve hours. Addition of alcohol facilitates the precipitation; free alkalis, on the other hand, retard its formation. The salts of lithium, ammonium, and the metals of the alkaline earths, give precipitates with potassium metantimonate, and hence these substances must be removed from solution before the above test for sodium can be applied.

Ammonium Antimonate, NH_4SbO_3, is formed by dissolving the acid in warm ammonia. It separates out on cooling as a crystalline powder, which is insoluble in water, and readily gives off ammonia. This is the only ammonium antimonate which is known.[2]

The antimonates of metals of the other groups are either difficultly soluble or insoluble in water. They may be obtained by double decomposition as crystalline precipitates, which are decomposed by weak acids with formation of acid salts, whilst stronger acids, on the other hand, liberate antimonic acid. Almost all the antimonates dissolve in strong hydrochloric acid.

[1] *Ber.* 1885, **18**, 2353. [2] Raschig, *Ber.* 1885, **18**, 2743.

Normal Lead Antimonate, $Pb(SbO_3)_2$, is a white curdy precipitate, insoluble in water. The *basic salt*, $Pb_3(SbO_3)_2(OH)_4 + 2H_2O$, occurs as bleinierite, at Nertschinsk, in Siberia, and Endellion, in Cornwall, in reniform or spheroidal masses, which possess a resinous appearance and a white, grey, brown, or yellowish colour. Another basic salt, which is used in oil painting under the name of Naples Yellow, is obtained by heating a mixture of one part of tartar emetic, two parts of lead nitrate, and four parts of common salt, for two hours to the fusing-point of chloride of sodium, and then lixiviating with water.

Antimony and the Halogens.

435 *Antimony Trifluoride*, SbF_3, is obtained as a dense snow-white mass, by distilling antimony with mercury fluoride. If a solution of the oxide in an excess of hydrofluoric acid be evaporated, the fluoride is also obtained in rhombic pyramids. It is deliquescent, and is not decomposed by water; but if the solution be evaporated without an excess of hydrofluoric acid a basic fluoride is formed. Antimony trifluoride forms fine crystalline double salts with the fluorides of the alkali-metals containing one molecule of the trifluoride to one, two, or three molecules of the alkali fluoride. The potassium salt is used in calico printing.

Antimony Pentafluoride, SbF_5, is obtained by dissolving antimonic acid in hydrofluoric acid. On evaporation a gummy mass remains which is decomposed on heating. It forms difficultly crystallisable double salts with the fluorides of the alkali-metals.[1]

436 *Antimony Trichloride*, $SbCl_3$.—"Basil Valentine" says, "Take of fine white, well-sublimed corrosive sublimate, and of good spiessglas the same quantity. Rub these up together and distil them. The oil which comes over is at first white, and congeals like ice or clots of butter." This preparation was termed *butyrum antimonii*, and was supposed to contain quicksilver until Glauber, in 1648, showed that this was not the case, inasmuch as it could be prepared by distilling spiessglas with oil of vitriol and common salt or hydrochloric acid. Several other methods of preparation may be mentioned, as, for example, by heating sulphate of antimony with sodium

[1] Marignac, *Annalen*, 1868, **145**, 239.

chloride, as well as by heating an excess of metallic antimony, or its sulphide, in a current of dry chlorine.

Antimony trichloride is a crystalline mass, melting at 73°·2 and boiling at 223°·5 (Thorpe). Its colourless vapour has the normal specific gravity of 7·8. On exposure to moist air the solid deliquesces to a clear liquid, and this, on evaporation over sulphuric acid, yields crystals of the anhydrous chloride. A solution of the chloride is best obtained by boiling the sulphide with strong hydrochloric acid. When this is distilled in a retort, water comes over first, next the excess of hydrochloric acid, and lastly, the anhydrous chloride. The concentrated solution, which has a specific gravity of 1·35, is known as *liquid butter of antimony*, and is employed for giving a brown surface to iron and steel wares, such, for instance, as gun-barrels (brown Bess); it is also sometimes used for pharmaceutical purposes. The anhydrous chloride yields with dry ammonia the brittle white compound $SbCl_3.NH_3$, which, on heating, gives off ammonia. It combines with hydrochloric acid to form the crystalline compound $2SbCl_3.HCl + 2H_2O$ and also forms soluble crystalline double salts with a variety of metallic chlorides.

Powder of Algaroth.—If the acid solution of the chloride be diluted with water, a white precipitate of the basic chloride is thrown down. This precipitate was known to Paracelsus, who employed it as a medicine, and states in his *Archidoxa* that in order to prepare it, corrosive sublimate is to be distilled with antimony, and the product coagulated with water, when the *mercurius vitæ* is obtained. Towards the end of the sixteenth century it was much employed, especially by the Veronese physician, Algarotus, and was termed by him *pulvis angelicus*, although it has been generally known as *powder of Algaroth*. The presence of tartaric or free hydrochloric acid prevents the precipitation of this substance. Its composition varies according to the method of its preparation. If ten parts of solid trichloride are mixed with seventeen parts of water, and allowed to stand until the precipitate has become crystalline, the compound SbOCl is deposited in small rhombohedra. These may be washed with ether in order to remove the excess of the chloride. The same compound is obtained by heating equal molecules of the trichloride and absolute alcohol in sealed tubes to 140°. If one part of the trichloride be mixed with three parts of water, and the precipitate filtered off quickly and mixed with ether, the same body is obtained in the form of

an amorphous powder. When this substance is heated the trichloride is given off, and the oxychloride, $Sb_4O_5Cl_2$, remains behind. The last named compound is formed as an amorphous precipitate when the chloride is mixed with from five to fifty parts of water; on standing, it gradually becomes crystalline, forming silky prisms. If three times its bulk of hot water be added to the trichloride, and the liquid allowed to stand at 60° for some hours, crystals are obtained resembling soda crystals, which also possess the composition $Sb_4O_5Cl_2$.[1] When larger quantities of water are employed still more basic chlorides are formed, and if these are boiled repeatedly with water, they are converted into the trioxide, this reaction taking place more quickly in the presence of sodium carbonate. If antimony oxide be dissolved in boiling antimony trichloride, a pearl-grey crystalline mass is obtained on cooling, having the composition $SbOCl + 7SbCl_3$, and this compound yields the substance $2SbOCl + Sb_2O_3$ on treatment with absolute alcohol.

Antimony Pentachloride, $SbCl_5$, was discovered by H. Rose in 1835, and is prepared by the direct union of antimony and chlorine, which takes place with evolution of light and heat. It is also readily formed by saturating the fused trichloride with chlorine gas. Antimony pentachloride is a yellow, fuming, disagreeably-smelling liquid, which solidifies in a freezing mixture forming crystals melting at −6°. It is readily volatile, partially decomposing on distillation into chlorine and trichloride, but under a pressure of 22 mm. it boils without decomposition at 79°, whilst under the same conditions the trichloride boils at 113°·5.[2] The vapour density under a pressure of 58 mm. at 218° is 10, the calculated number being 10·3.[3] When brought in contact with the requisite quantity of ice-cold water it forms the monohydrate $SbCl_5 + H_2O$, crystallising from chloroform in thin deliquescent scales melting at 90°.[4] If more water be added a clear liquid is obtained, and this, on standing over sulphuric acid, deposits crystals of $SbCl_5 + 4H_2O$,[5] which are insoluble in chloroform (Anschütz and Evans). Hot water produces antimonic acid. As it easily loses chlorine, antimony pentachloride is employed in organic chemistry in the chlorin-

[1] Sabanajew, *Zeitsch. Chem.* 1871, 204.
[2] Anschütz and Evans, *Ber.* 1886, **19**, 1994.
[3] Anschütz and Evans, *Annalen*, 1889, **253**, 95.
[4] Anschütz and Evans, *Annalen*, 1887, **239**, 239.
[5] Weber, *Annalen*, 1863, **125**, 86.

ation of many bodies, since by its successive formation and decomposition it acts as a chlorine carrier. With hydrocyanic acid it forms the white crystalline compound $SbCl_5 + 3HCN$, which volatilises under 100° with partial decomposition. It also forms solid compounds with various chlorides and oxides, such as $SbCl_5 + SCl_4$, $SbCl_5 + PCl_5$, $SbCl_5 + POCl_3$, $2SbCl_5 + 5NOCl$, $2SbCl_5 + NO$, $3SbCl_5 + 2NO_2$.

When three molecules of antimony pentachloride are heated with one molecule of pentoxide to 140°, two oxychlorides are obtained, viz., Sb_3OCl_{13} and $Sb_3O_4Cl_7$, which, as they melt at different temperatures, can be separated one from the other. The first is a white crystalline extremely deliquescent mass, which melts at 85°, whilst the other forms yellowish crystals, which melt at 97°·5.

437 *Antimony Tribromide*, $SbBr_3$.—Powdered antimony combines directly with bromine with evolution of light and heat. The tribromide sublimes in colourless deliquescent needles, which melt at 95°, and boil at 275°; water decomposes it with formation of a basic bromide. Another method of preparation consists in heating an excess of powdered antimony with a solution of bromine in carbon bisulphide; the tribromide thus obtained on evaporation crystallises in octohedra.

A pentabromide does not appear to exist.

438 *Antimony Triiodide*, SbI_3.—These elements combine together directly with evolution of so much heat that if large quantities are employed explosions may ensue. The tri-iodide is thus obtained as a brownish-red crystalline mass, yielding a cinnabar-red powder, and crystallising in six-sided tablets from solution in hot carbon bisulphide. It melts at 171° to a garnet-red liquid, and forms a violet-red vapour, which at a higher temperature becomes scarlet. It sublimes at a temperature slightly above its melting-point, boils between 414–427° (Carnelley and Williams), and is decomposed by water, with formation of a yellow oxyiodide, which forms crystalline double salts with the various iodides.

Antimony Pentiodide, SbI_5, is said to be formed as a very unstable brown crystalline mass when the two elements are fused together and the excess of iodine removed by heating at 130°.[1]

[1] Pendleton, *Chem. News*, 1883, **48**, 97.

Antimony and the Sulphur Group.

439 Only two well defined sulphides of antimony, the trisulphide, Sb_2S_3, and the pentasulphide, Sb_2S_5, are known. A tetrasulphide, Sb_2S_4, has been described, but its existence is doubtful.[1]

Antimony Trisulphide, Sb_2S_3, occurs crystallised as stibnite in the older stratified rocks. This is the most important ore of antimony, and it is found in considerable quantity, occurring in Cornwall, Hungary, Transylvania, in the Banat, in the Harz, in Westphalia, in the Black Forest, in Bohemia, in the Auvergne, in Estramadura, Algiers, Corsica, Siberia, Nevada, New Brunswick, in Japan, where it is found in magnificently large and perfect crystals, and especially, in large quantities, in Borneo. It crystallises in prisms, but is usually found in columnar or striated masses, which soil the fingers like graphite. It is easily pulverisable, and readily fusible, and has a specific gravity of 4·62. The crude sulphide occurring in commerce is obtained by melting the ore in the manner already described, and is sold in rounded masses having the form of the vessel in which the molten sulphide solidifies. It has a metallic lustre, steel-grey streak, and crystalline fracture. From early times this substance has been used in the East under the name of Kohl. The alchemists occupied themselves much with the properties of this body, as it was used for the purification of gold, and was termed *judex ultimus*, or *lupus metallorum*. Antimony trisulphide also exists in the amorphous state, and in this form was known to "Basil Valentine." He states that crude spiessglas may be sublimed with formation of a red body when it is mixed with *sal ammoniacum*. In this way antimony chloride and ammonium sulphide are formed, which again react on cooling, producing the original compounds, the antimony sulphide separating out as a red powder. Glauber, and also Lemery, speak of the solution and the subsequent precipitation of the spiessglas with caustic alkalis; but it was not until 1714 that attention was directed to the red sulphide of antimony. In the above year a Carthusian monk whose life had been despaired of by the Paris faculty, was saved by a monk of the name of Simon administering to him a medicine which was first prepared by a German apothe-

[1] See Bosek, *Journ. Chem. Soc.* 1895, 1, 515.

cary, a disciple of Glauber, and which was bought by the Parisian apothecary De la Ligérie. This was soon known as the "poudre des chartreux" or Carthusian powder. Simon, however, gave to it the name of *Alkermes mineral*, and such was the reputation which this medicine enjoyed that the French Government bought the receipt for its preparation in 1720 from De la Ligérie. The process consisted in boiling the spiessglas with potashes and allowing the clear solution to cool when the kermes was deposited as a red powder. In 1728 Stabel found that when caustic potash was employed, a red powder was also obtained, which Mender in 1738 showed to be the pure kermes, and C. J. Geoffroy in 1735 proved that the same preparation was obtained when spiessglas was fused with carbonates of the alkali-metals, and the liver of antimony thus obtained boiled with water. This body was believed to be a compound of antimony, sulphur, and alkali, though chemists such as Baumé denied that it contained any alkali, and assumed that in spiessglas regulus of antimony was combined with sulphur, whilst in mineral kermes calx of antimony was combined with sulphur. Many other views were held concerning the composition of this compound until Rose in 1825, and Fuchs in 1833, showed that mineral kermes is nothing more than amorphous antimony sulphide.

Various methods may be employed for the preparation of mineral kermes, which for fifty years was highly prized as a medicine, and even now is sometimes employed. All these processes yield a preparation containing, as impurity, varying quantities of antimony oxide, both free and combined with the alkalis. Hence the preparations of the kermes should be carried on exactly according to the prescription of the pharmacopœia.

In order to prepare the amorphous sulphide free from oxide, the crystalline compound is boiled with caustic potash in absence of air, the liquid filtered and the hot diluted solution precipitated with sulphuric acid. The precipitate is then washed with very dilute acid, and afterwards with cold water; and to remove any oxide which may be present it is heated with a solution of tartaric acid. Thus obtained the precipitate becomes anhydrous when dried at 100° and forms a reddish-brown light powder which readily soils the fingers. This is more soluble in hydrochloric acid, in the fixed alkalis, and their carbonates than the crystalline compound into which it is converted on fusion. It

may also be obtained by pouring fused stibnite into an excess of cold water. It then forms an amorphous lead-grey mass which appears of a hyacinth-red colour when seen in thin films, has a specific gravity of 4·15, and when triturated is converted into a dark reddish-brown powder.

If sulphuretted hydrogen be passed into an acid solution of the trichloride or into an acidified solution of tartar-emetic, an orange-red precipitate of amorphous hydrated sulphide is obtained, which after drying at 100°–130° becomes black at 200°. The precipitated sulphide also becomes black when it is boiled with two parts of hydrochloric acid and one of water in a current of carbonic acid gas.[1]

When a dilute solution of tartar-emetic is added to sulphuretted hydrogen water, a colloidal solution of antimony sulphide is produced which is orange-red by transmitted light, and can be boiled without undergoing change. Calcium chloride and many other salts cause an immediate precipitation of the sulphide.[2] On heating in a current of hydrogen the trisulphide is reduced to metal, but it may be sublimed without decomposition in an atmosphere of nitrogen. Crystalline antimony sulphide is used not only for the preparation of the other antimony compounds, but also in pyrotechny, and for the preparation, especially in Sweden, of the heads of lucifer matches, as well as for the composition used for firing breechloading firearms. The amorphous sulphide is largely used as a means for vulcanising caoutchouc, to which it also imparts a reddish-brown colour.

The compound known as *antimony cinnabar*, which is obtained by warming a solution of the trichloride with sodium thiosulphate, is the trisulphide. This substance is used in oil-painting as well as in water-colour painting and as a distemper.

The Thioantimonites or *Livers of Antimony* are formed by the combination of the trisulphide with basic sulphides. Those of the alkali metals are prepared by fusing the constituents together. They are brown or black, and when they contain a large quantity of basic sulphide they are easily soluble in water, but when the quantity of antimony increases, these livers of antimony become more difficultly soluble, and at last insoluble in water. The same compounds are formed when the trisulphide is dissolved in an aqueous solution of a sulphide, or, mixed

[1] Mitchell, *Chem. News*, 1893, **67**, 291.
[2] Picton, *Journ. Chem. Soc.* 1892, i. 142.

with antimonite, when the trisulphide is fused with an alkali or alkali carbonate:

$$2Sb_2S_3 + 4KOH = 3KSbS_2 + KSbO_2 + 2H_2O.$$

Acids precipitate the amorphous trisulphide from these solutions, which also absorb oxygen rapidly from the air. Many of the thioantimonites occur as minerals, and the composition of some of these has been already given.

440 *Antimony Pentasulphide*, Sb_2S_5.—This compound does not occur in the native state. "Basil Valentine" mentions that when spiessglas is boiled with strong caustic ley, and acetic acid added to the liquor a red body is precipitated, and Quercetanus in 1603 mentions in his pharmacopœia a preparation from spiessglas and liver of sulphur by means of acids, terming it *sulphur antimonii auratum*. In 1654 Glauber mentions in the "pharmacopœia spagyrica" the preparation obtained by precipitating the slag formed in the preparation of regulus of antimony by means of acetic acid, and recommends this product as *panacea antimonialis* or *sulphur purgans universale*. This preparation, which was known as golden sulphuret of antimony, soon became a favourite medicine. It was obtained from the more or less oxidised solution of liver of antimony, containing a thioantimonate. If this be fractionally precipitated by hydrochloric acid, a brown kermes is first thrown down and afterwards a golden coloured sulphide, which has therefore been termed *sulphur auratum tertiæ præcipitatonis*. In later times stibnite was boiled with alkali with addition of sulphur and the solution precipitated with acid. At the present day pure thioantimonate is first prepared, and for this purpose the well-crystallised sodium salt is employed; this is dissolved in from 10 to 60 parts of water and a cold mixture of 3·3 parts of sulphuric acid and 100 parts of water is gradually added; the precipitate is well washed with distilled water and dried at a moderate temperature in the dark.

The pure pentasulphide is precipitated when an excess of sulphuretted hydrogen water is added to a solution containing the antimony in the form of antimonic acid at the ordinary temperature (Bunsen).[1] When sulphuretted hydrogen is passed into the antimony solution a mixture of pentasulphide, trisulphide, and sulphur is formed, the proportion of the pentasulphide diminishing as the rate at which the gas is passed is

[1] *Annalen*, 1878, **192**, 305.

lessened and as the temperature is raised. Hydrochloric acid up to about 20 per cent. favours the production of the pentasulphide, but in larger amount hinders it.[1]

Antimony pentasulphide is a fine yellowish-red powder easily soluble in aqueous alkalis and their sulphides, and also, in absence of air, in warm ammonia. It likewise dissolves in the carbonates of the alkali metals, but not in ammonium carbonate. When exposed to the sunlight, heated in water to 98°, or simply heated in absence of air, it decomposes into the black trisulphide and sulphur, and when boiled with hydrochloric acid, sulphur separates out, sulphuretted hydrogen is evolved, and the trichloride is found in solution.

Sodium Thioantimonate, $Na_3SbS_4 + 9H_2O$.—This is termed, from the discoverer, *Schlippe's salt*, and is obtained by dissolving the trisulphide, sulphur, and caustic soda or a mixture of soda ash and lime, in the requisite quantity of water; or by fusing together 16 parts of anhydrous sodium sulphate, 13 parts of stibnite, and 5 parts of carbon, dissolving, and boiling the solution with 2·5 parts of sulphur. It crystallises in large colourless or yellow regular tetrahedra which have an alkaline reaction and a saline cooling metallic taste resembling that of liver of sulphur. It dissolves at 15° in 2·9 parts of water and is precipitated from aqueous solution by alcohol. The hydrated crystals on exposure to moist air soon become covered with a kermes-coloured coating, and when they are heated in absence of air water is given off and the anhydrous salt formed. This fuses at a dark red-heat yielding on solidification a soluble brown mass.

Potassium Thioantimonate, $K_3SbS_4 + 9H_2O$, is prepared in a similar way to the sodium salt and forms deliquescent crystals.

Barium Thioantimonate, $Ba_3(SbS_4)_2 + 6H_2O$, is prepared by dissolving the freshly precipitated golden sulphide of antimony in barium monosulphide and precipitating by alcohol. In this way groups of stellated needles are obtained.

The *calcium* salt is prepared in a similar way and is thrown down as an oily liquid on addition of alcohol.

The thioantimonates of the other groups are almost entirely insoluble in water and are obtained by double decomposition between their soluble salts and sodium thioantimonate. They are yellow, red, brown, or black precipitates.

Antimony Oxysulphide, Sb_2S_2O, is found, together with

[1] Boseĕk, *Journ. Chem. Soc.* 1895, 1, 515; Brauner, *Journ. Chem. Soc.* 1895, 1, 527.

stibnite, as kermesite or antimony blende in needle-shaped crystals or thin six-sided prisms which have a cherry-red colour and an almost metallic lustre. The same compound is obtained as a reddish-brown powder by adding antimony trisulphide to fused antimony iodide, and treating the mass with dilute hydrochloric acid, when a dark reddish-brown lustrous powder of antimony thioiodide, SbSI, remains behind, and this, when boiled with water and oxide of zinc, is converted into the oxysulphide.

Both the following preparations, which were formerly made use of, are probably mixtures of the oxide and sulphide, as was shown by Proust in opposition to the view held by Berthollet that they were compounds of the oxide with varying amounts of sulphur.

Glass of Antimony or *vitrum antimonii* is obtained by fusing oxidised stibnite with a small quantity of the sulphide. It forms a transparent dark ruby-red mass, formerly largely employed for obtaining the other antimony compounds, but now, however, only used for imparting a yellow tint to glass and porcelain.

Antimonial Saffron or *crocus antimonii.*—If stibnite be deflagrated with a quantity of saltpetre insufficient for complete oxidation, a brownish-yellow powder is obtained on lixiviation which when heated melts to a yellow glass.

Chlorosulphide of Antimony.—Two compounds of this class, SbS_2Cl and Sb_2S_5Cl, have been obtained as reddish-brown crystalline substances by the action of sulphuretted hydrogen on antimony trichloride at its melting point.[1] The compound, $SbSCl + 7SbCl_3$, is obtained by heating the trichloride and trisulphide together. Alcohol converts it into $2SbSCl + 3Sb_2S_2$.

Iodosulphide of Antimony.—Compounds of the formulæ SbS_2I and SbS_2I_3, are formed when antimony trisulphide is heated with iodine (Ouvrard).

Antimony Trisulphate, $Sb_2(SO_4)_3$, is obtained as a white mass by heating either the metal or the oxide with concentrated sulphuric acid. The composition of the salt depends on the concentration of the acid used, acid or basic salts being obtained when the acid employed is stronger or weaker than that represented by the formula H_2SO_4.[2] The normal salt crystallises from a tolerably acid concentrated solution in long glistening

[1] Ouvrard, *Compt. Rend.* 1893, **116**, 1516; **117**, 107.
[2] Adie, *Chem. News*, 1890, **61**, 58.

silky needles,[1] and is decomposed by water into a soluble acid salt, and an insoluble basic salt. If antimony chloride be heated with fuming sulphuric acid, a basic salt, $Sb_2O(SO_4)_2$, is produced in small glistening crystals, which in contact with alcohol are transformed into the salt $Sb_2O_2SO_4$, consisting of a white powder, which, when treated with boiling water, yields the salt $Sb_4O_5SO_4$. Several other salts have also been described.

441 *Antimony Triselenide*, Sb_2Se_3, is formed when the two elements are fused together, a metallic lead-grey crystalline mass being produced. When selenium hydride is passed into a solution of tartar emetic, the same compound is precipitated as a black powder.

Antimony Pentaselenide, Sb_2Se_5, is precipitated as a brown powder by adding dilute sulphuric acid to a solution of sodium seleno-antimonate.

Sodium Seleno-antimonate, $Na_3SbSe_4+9H_2O$, is isomorphous with the corresponding thio-antimonate, and is obtained by fusing together 4 parts of sodium carbonate, 6 parts of antimony triselenide, 3 parts of selenium, and 1 of charcoal. The fused mass is boiled out with water in absence of air and the filtrate covered with a layer of strong alcohol. The salt separates out after some time in orange-red transparent tetrahedra which are soluble in two parts of cold water and become red-coloured on exposure to air, with separation of selenium. When a solution of Schlippe's salt is boiled with selenium, filtered, and the solution concentrated in absence of air, yellow tetrahedra of $Na_3SbSeS_3+9H_2O$ are deposited.

Antimony and tellurium when fused together yield, according to the proportions employed, either an iron-grey metallic lustrous mass, or a tin-white *antimony tritelluride*.

Antimony and the Nitrogen Group.

442 No definite nitrate of antimony is known, although the white powder obtained by the action of nitric acid on antimony contains nitrogen and is converted by water into antimony pentoxide and nitric acid.

If *phosphorus* be added to fused antimony, a tin-white phosphide of antimony is obtained which when heated in the air burns with a greyish flame.

[1] Schultz-Sellack, *Ber.* 1871, **4**, 13.

Antimony Thiophosphate, $SbPS_4(Sb_2S_3 + P_2S_5)$, is formed when the trichloride or trisulphide is heated with phosphorus pentasulphide. It is a fusible, insoluble yellow crystalline mass.[1]

Antimony combines directly with *arsenic*. The compound $SbAs_3$ occurs as allemontite in reniform or amorphous masses having a metallic lustre.

Medicinal Uses of Antimony.

443 As we have seen, various antimony preparations are used as important medicines. Paracelsus was one of the first to employ these for inward use, and his example was followed by the other iatro-chemists, many of whom worked diligently on antimony and its compounds. The disciples of the old Galenic school were violently opposed to the introduction of the antimony compounds into medicine, and they succeeded in inducing the Paris Parliament in 1566 to prohibit the use of antimony and its compounds by all physicians on pain of having their licenses withdrawn. In 1603 the medical faculty of Paris took a similar step, and this decree was not withdrawn until the year 1666.

Metallic antimony itself was at one time employed for the preparation of goblets in which wine was allowed to stand overnight in order that it might be used as an emetic; but this practice fell into disuse even during Boyle's time. Pills made of metallic antimony were employed at a later period: these were termed everlasting pills, because they, like the goblets, were believed only to act by contact and not to lose their weight. This error was first combated by Lemery and Vigani, a Veronese quack doctor who lived in England, and they showed that both antimony and fused stibnite became acted upon when placed in contact with wine.

Whilst formerly a large number of antimony compounds were employed in medicine, the only ones which are used at the present day are tartar emetic or potassium antimonyl tartrate, $C_4H_4K(SbO)O_6$; and the trisulphide or *antimonium sulphuratum*. The first compound is given in doses of $\frac{1}{16}$ to $\frac{1}{8}$ of a grain as a diaphoretic, and from 1 to 2 grains as an emetic. The dose of the second is from 1 to 5 grains.

In larger doses it produces, like white arsenic, violent irrita-

[1] Glatzel, *Ber.* 1891, **24**, 3886.

tion in the intestines, vomiting and purging. When one large dose only is administered, the case proceeds rapidly to recovery or death, the former generally, if the case is placed early under proper treatment, and in this respect acute antimonial is distinguished from acute arsenical poisoning.

In cases of chronic antimonial poisoning the principal symptoms are great nausea, vomiting of mucous and bilious liquids, great depression, purging, and finally death from complete exhaustion. Several cases have occurred in this country to show that tartar emetic has been thus criminally and fatally used (Taylor).

Detection and Estimation of Antimony.

444 When a small quantity of an antimony compound is heated in the upper reduction zone of a Bunsen burner on a thread of asbestos the flame becomes of a bluish tinge, and when a small porcelain basin filled with cold water is held above it a brownish-black deposit of metallic antimony is found upon the basin, and this is but slightly attacked by cold nitric acid, and is insoluble in sodium hypochlorite. Arsenic gives a very similar reaction (see vol. i. p. 637), but this may be distinguished from antimony by the fact that during the reduction a garlic-like smell of arsenic is noticed, and the metallic film is readily soluble in sodium hypochlorite. If an antimony compound be heated on a carbonised match, a brittle metallic bead is obtained, whilst arsenic is completely volatilised. Most of the antimony compounds are insoluble in water, but dissolve in hydrochloric acid. Those which do not thus dissolve may be obtained in solution by fusion with potassium carbonate and saltpetre, and subsequent solution in hydrochloric acid. Sulphuretted hydrogen produces in acid solutions a very characteristic orange-red coloured precipitate of antimony trisulphide. If other metals precipitable by sulphuretted hydrogen be present, the mixed sulphides, after washing, are treated with ammonium sulphide, filtered, and the filtrate acidified with hydrochloric acid. This precipitate may contain, together with antimony, the sulphides of tin and arsenic. This last metal is removed by digesting with freshly prepared solution of ammonium carbonate, and washing the residue with water. This is then brought into solution by heating with hydrochloric acid, and the liquid is placed in a

platinum dish containing a piece of zinc; the antimony is deposited upon the platinum as a black adherent coating, which is readily soluble in nitric acid. If the nitric acid solution be evaporated with some hydrochloric acid, diluted with water, and treated with sulphuretted hydrogen, the characteristic precipitate of antimony sulphide is obtained. The stain also dissolves in ammonium sulphide, forming a solution which leaves an orange-coloured residue on evaporation.

Antimony may also be detected by means of Marsh's test carried out as described under arsenic (vol. i. p. 637). The mirror obtained is deposited much closer to the flame than that of arsenic, is formed at a lower temperature, does not yield a crystalline deposit of oxide when heated in the air, and is not soluble in sodium hypochlorite. When the gas is passed into silver nitrate solution, silver antimonide is precipitated (p. 781).

Antimony trichloride gives a spark-spectrum containing among others the following lines mentioned in order of their relative brightness (Lecoq de Boisbaudran):

α 6005 β 5568 γ 6130 δ 6079

Antimony is usually estimated either as the sulphide or the tetroxide. In the first case it is obtained as a hydrated precipitate, which may also contain sulphur and pentasulphide. It is necessary, therefore, to dry this at 100°, to weigh it, and to bring a known fraction into a porcelain boat contained in a glass tube. Through the tube dry carbon dioxide is passed, and the sulphide heated, the pure anhydrous trisulphide remaining behind. The sulphide may also be oxidised by means of nitric acid and the residue ignited and weighed as tetroxide, or it may be dissolved in a large excess of sodium sulphide, and the resulting solution electrolysed and the metal weighed.[1] Antimony is also frequently estimated volumetrically, the trioxide, in presence of sodium bicarbonate, being converted by means of standard iodine solution into the pentoxide.

The *quantitative* separation of antimony from other metals with the exception of arsenic and tin, does not exhibit any difficulty. Should these three elements be present together their sulphides must be first converted into oxides by treatment with nitric acid, and these fused for some time with eight times their weight of caustic soda. The cooled mass is next allowed to soften in hot water until the sodium metantimonate has

[1] Kohn and Barnes, *British Assoc. Reports*, 1896, 244.

separated out as a white powder, and then one volume of alcohol of specific gravity 0·83 is added for every three volumes of the liquid. After standing for some time the liquid is filtered and the precipitate well washed with dilute alcohol, to which at last some caustic soda is added. The filtrate contains the stannate and arsenate, whilst the whole of the antimony is contained in the residue, and this is converted in the usual way into the sulphide (H. Rose). A more rapid method of separation depends on the fact that in presence of free oxalic acid antimony is precipitated by sulphuretted hydrogen as the sulphide, whereas tin remains in solution.[1]

The separation of antimony from arsenic which had previously been difficult and unsatisfactory, was first rendered exact by Bunsen. The moist and well-washed mixture of sulphides obtained by precipitation with sulphuretted hydrogen is dissolved on the filter by an excess of caustic potash, and the diluted solution heated with chlorine until all the free alkali has combined. The excess of chlorine is then got rid of by repeated evaporation with hydrochloric acid, the solution diluted, and this heated with a freshly prepared solution of sulphuretted hydrogen until all the antimony is precipitated. A rapid current of air is then passed through the liquid in order to expel the excess of sulphuretted hydrogen, and the precipitate washed first with water, then with alcohol, and at last repeatedly with carbon bisulphide, in order to remove free sulphur. After drying at 110° pure pentasulphide of antimony remains, and this is afterwards weighed. The arsenic in the filtrate may be estimated by subsequent continued treatment with sulphuretted hydrogen when the pentasulphide is precipitated, and treated as above described.

A still simpler method of effecting this separation consists in adding ferrous sulphate or chloride to a solution of the chlorides of the two metals in hydrochloric acid, saturating with hydrochloric acid gas and distilling. The whole of the arsenic passes over and may be collected in dilute hydrochloric acid, whilst the antimony remains behind and may be precipitated in the usual way after the ferric salt has been reduced to the ferrous state.[2]

445 *Atomic Weight.*—The methods which have at various times been employed for the determination of the atomic weight

[1] F. W. Clarke, *Chem. News*, 1870, **21**, 124; Lesser, *Zeit. Anal.* 1888, **27**, 218; Warren, *Chem. News*, 1890, **62**, 216; J. Clark, *Journ. Chem. Soc.* 1892, i. 424.

[2] E. Fischer, *Ber.* 1880, **13**, 1778.

of antimony have led to somewhat divergent results. The number 128, which was obtained by Berzelius by the oxidation of the metal with nitric acid, was long accepted as correct, until Schneider's [1] experiments on the reduction of the sulphide proved that 119·7 was nearer the truth. Dexter [2] then found the number 121·1 by the treatment of the metal and trioxide with nitric acid, the resulting oxide being converted into the tetroxide by ignition. This was confirmed by Kessler,[3] who adopted the same plan, but effected the oxidation volumetrically by means of an acid solution of potassium chlorate, and by Dumas [4] who analysed the trichloride. On the other hand, a very carefully conducted series of analyses of the bromide led Cooke [5] to the number 119. Still more recently the electrolysis of the chloride has led in the hands of Pfeifer [6] and of Popper [7] to the number 120·4.

The most probable value may perhaps be taken as 119·4 (O = 15·88).

BISMUTH, Bi = 207

446 The word *marcasite* by which, up to recent times, the metal bismuth was often designated, is found in the authors of the thirteenth century. Hence it has been supposed that this metal was known at that time. This is, however, not the case, for the name marcasite had in those days, and even at a much later period, a very indefinite meaning, being given to any ore which had a metallic appearance, and especially to those ores which are now classed as pyrites.

Bismuth was classed by Paracelsus amongst the semi-metals. On the other hand, Agricola mentions *bisemutum* or *plumbum cinereum*, as a true metal which is usually added to tin in order to make it work better. Notwithstanding this clear statement, it was subsequently confounded by Libavius with antimony, and by Lemery with zinc. Metallic bismuth was moreover described by "Basil Valentine" in his Last Testament: "Antimonium must be placed between tin and lead, as

[1] *Pogg. Ann.* 1856, **98**, 293.
[2] *Pogg. Ann.* 1857, **100**, 563.
[3] *Ann. Chim. Phys.* 1859 [3], **55**, 129.
[4] *Pogg. Ann.* 1861, **113**, 145.
[5] *Sill. Amer. Journ.* [3], **15**, 41 and 107.
[6] *Annalen*, 1881, **209**, 173.
[7] *Annalen*, 1886, **233**, 153.

bismuth or magnesia is placed under and between tin and iron," and he also states that "bismuth or marcasite is a bastard *jovis*." Pott, in 1739, was the first to make us acquainted with the special properties of bismuth, and its reactions were exactly studied by Bergman.

Bismuth is a comparatively rare metal. It is found chiefly in the native condition, but also as the oxide or bismuth ochre, Bi_2O_3; less frequently it occurs as bismuthite, Bi_2S_3, whilst it is found still more sparingly in the following minerals: telluric bismuth, or tetradymite, Bi_2Te_3; emplectite, $Cu_2Bi_2S_4$; bismutite, $3(BiO)_2CO_3+2Bi(OH)_3+3H_2O$; aikinite, $(Pb,Cu_2)_3Bi_2S_6$; pucherite, $BiVO_4$; eulytine or bismuth silicate, $Bi_4(SiO_4)_3$, &c.

447 *Native bismuth* is sometimes found nearly pure. Usually, however, it contains other metals alloyed with it, or it is mixed with a variety of ores, as is shown by the following analyses:—

Analyses of Native Bismuth.

Locality.	Peru.		Dalekarlein in Sweden.	
Analyst . .	Genth.	Forbes.	Cleve.	Feilitzen.
Bismuth .	99·914	94·46	95·16	91·15
Iron . .	trace	—	1·80	4·03
Copper .	—	—	trace	trace
Gold . .	—	trace	—	—
Sulphur .	—	0·07	1·42	2·28
Tellurium.	0·042	5·09	—	—
Arsenic .	—	0·38	—	—
Silica . .	—	—	0·23	0·34

448 The chief sources of bismuth[1] are the Saxon smalt works, in Oberschlema and in Pfannenstiel, where the bismuth occurs at Schneeberg. Formerly bismuth was obtained by simply heating the ore in sloping iron tubes. In this way merely that portion of the metal present in the native state was obtained, and this only in a very incomplete manner. The residue was employed in the manufacture of smalt, and the bismuth again

[1] Winkler, *Ber. Entw. Chem. Ind.* i. 953.

extracted from the cobalt-speiss. At the present day all bismuth ores are roasted and afterwards smelted in the pots of the smalt furnaces with the addition of iron, carbon, and slag. Two layers are thus obtained, the upper one consisting of the cobalt-speiss, the lower being almost pure bismuth, which, owing to its low melting-point, can be drawn off in the liquid state after the upper layer of speiss has solidified. The crude bismuth thus obtained, only contains small traces of iron, cobalt, nickel, lead, silver, sulphur, and arsenic, and is purified by melting it on a slightly inclined iron plate, under which a wood fire is made, so that the bismuth melts and runs down. In this way almost chemically pure refined bismuth is obtained; it is then cast into semi-circular moulds in masses weighing from 10 to 12 kilos., and thus sent to market. In Freiberg, where ores of lead and silver containing bismuth are worked, the bismuth collects as an oxide in the refining of the silver in the slag of *blicksilber*. This often contains from 5 to 20 per cent. of bismuth, which is then extracted by solution in cold hydrochloric acid, and the solution diluted with water, until it becomes turbid. The liquors are allowed to stand till clear, and then a sufficient quantity of water added to precipitate the whole of the bismuth as basic salt. This is then fused with soda-ash and coal, and the fused metal cast into bars.

In Altenburg, bismuth is also obtained in the wet way from the roasted tin slags, and in France the ore occurring at Meymac is treated with hydrochloric acid, the bismuth precipitated by iron, and afterwards reduced by carbon. Bismuth was also formerly reduced at Joachimsthal, but now the ore is sent to Saxony to be smelted.

A considerable amount of foreign bismuth is worked up in England at the Magnesium Works at Patricroft. Some comes from Adelaide in South Australia, some from Bolivia and Peru. The ore there occurs very high up in the Andes. Thus one Peruvian ore containing 5 per cent. of tellurium occurs, according to David Forbes, at an elevation two-thirds that of Illampu, the highest point of the chain of 25,000 feet; and a bismuth sulphide containing antimony is found in Bolivia, at a height of 19,000 feet, near the mountain Chovolque in the province of Chichas.

The total production of bismuth amounts to about 25,000 kilograms per annum. Of this about 18,000 kilos. come from Saxon works; 2,500 from Freiberg; 2,500 from England; 1,500

from Johanngeorgenstadt, and 500 from Altenberg. The quantity obtained in France from 1867 does not appear to amount to above a few hundreds of kilos. The composition of commercial bismuth is seen from the following table:

Analyses of Commercial Bismuth.

	Saxon Bismuth.	Bismuth from Joachimsthal.	Peruvian Bismuth.
Bismuth . . .	99·79	99·32	93·37
Iron	0·02	trace	2·058
Copper . . .	0·03	trace	
Lead	0·08	0·30	—
Silver . . .	0·07	0·38	—
Antimony . .	—	—	4·57
Tin	—	—	
Sulphur . . .	—	—	—

Bismuth which contains one or more per cent. of lead melts at a much lower temperature than pure bismuth. Such an impure metal exhibits on cooling the peculiarity that the solid crust of pure crystallised bismuth is seen to be broken through by drops of a liquid alloy, and this property has been employed to separate bismuth from lead (Matthey). Silver behaves in a similar manner. Commercial bismuth frequently contains small quantities of gold, which, along with silver, may be removed by melting with 2 per cent. of zinc and skimming off the surface layer, which is found to contain the precious metals.[1]

When bismuth is required for pharmaceutical purposes it is necessary to separate traces of arsenic which it sometimes contains. For this purpose it is melted with nitre or other oxidising agent, or fused with metallic-iron. The arsenic is also removed when the molten metal is well stirred and exposed to the air, any antimony being simultaneously oxidised.[2]

Herapath,[3] who found a small quantity of thallium in certain bismuth preparations, recommends that the bismuth salts which are to be employed for medicinal purposes should be boiled with caustic soda solution, the residue well washed with water, dissolved in nitric acid, and the basic nitrate precipitated by the addition of an excess of water. From this the other preparations of the metal can be obtained.

[1] Matthey, *Proc. Roy. Soc.* 1887, **42**, 89.
[2] Matthey, *Proc. Roy. Soc.* 1893, **52**, 46.
[3] *Pharmaceutical Journal*, **4**, 302.

In order to prepare chemically pure bismuth, the commercially pure metal is dissolved in nitric acid and evaporated with hydrochloric acid. The chloride is then dissolved in hydrochloric acid and the solution mixed with alcohol, which precipitates the greater portion of the lead in the form of chloride. The filtrate is poured into water and the precipitated oxychloride washed, redissolved in hydrochloric acid, and again precipitated with water, this process being frequently repeated. The oxychloride is then again dissolved in hydrochloric acid and precipitated with ammonia and ammonium carbonate, this operation being repeated three times, after which it is finally reconverted into oxychloride, and the latter reduced to metal by fusion with potassium cyanide. The metal thus obtained still contains lead, from which it can only be freed by electrolysis. For this purpose it is dissolved in nitric acid and the solution slowly electrolysed, any lead being deposited as peroxide on the positive pole. The bismuth is then finally fused with potassium cyanide.[1]

449 *Properties.*—Bismuth is a hard brittle metal, having a bright metallic lustre and a greyish-white colour, with a distinctly reddish tinge. Its specific gravity at 15° is 9·747 : it melts at 264°, and expands in the act of solidification, the specific gravity of the solid at the temperature of the melting point being 9·673 and that of the liquid 10·004.[2] Its boiling point lies between 1090° and 1450° (Carnelley and Williams), and it can be distilled in a current of hydrogen. The vapour density between 1600—1700° is about 11, a number which is intermediate between the values corresponding to the formulæ Bi and Bi_2.[3] When a large quantity is melted, allowed slowly to cool until the surface begins to solidify, the crust then broken, and the liquid metal poured out, fine large crystals are obtained. These are obtuse rhombohedra which have the appearance of cubes as their angles approach closely to 90°. They oxidise in the air, and frequently become covered with an iridescent film of oxide. The same colours may be obtained when the metal is melted in the air, but if the heat be continued, the metal gradually becomes altogether converted into oxide; at a red-heat steam is slowly decomposed by bismuth. This metal combines also directly with the elements of the

[1] Classen, *Ber.* 1890, **23**, 940.
[2] Vincentini, *Journ. Chem. Soc.* 1891, ii. 518.
[3] Meyer, *Ber.* 1889, **22**, 726.

chlorine group and with sulphur; hydrochloric and sulphuric acids do not act upon it in the cold, but the latter acid dissolves it on heating with evolution of sulphur dioxide. The best solvents for bismuth are nitric acid and aqua-regia, both of which dissolve the metal readily in the cold.

Bismuth serves for the preparation of many pharmaceutical products and cosmetics, and is also employed for the manufacture of alloys of low melting point, and in the construction of thermopiles.

450 *Alloys of Bismuth.*—Bismuth forms a number of alloys of low melting-point, which are known by the general name of fusible metal. The temperature of the melting-point depends on the proportion of the constituents as is shown in the following table :—

	Newton's Metal.	Rose's Metal.	Lichtenberg's Metal.	Wood's Metal.
Bismuth .	8	2	5	4
Lead . .	5	1	3	2
Tin . . .	3	1	2	1
Cadmium .	0	0	0	1
Melting-point	94°·5	93°·75	91°·6	60°·5

The melting-point can be still further reduced by the addition of mercury. Fusible metal is now largely used for stereotyping, obtaining copies of wood-cuts, &c., and is not only valuable on account of its low melting-point, but also because it expands considerably in the act of solidification, and thus gives a perfect cast; it is important to make the cast when the metal is so far cooled that it is beginning to be viscid. If any of these liquid alloys be poured into a glass vessel, this flies to pieces when the metal cools. Bismuth is also used in the manufacture of solder, and the soldering can be effected under hot water when a few drops of hydrochloric acid have been added. Alloys of lead, tin, and bismuth mixed together in such proportion that the mixture fuses at some particular temperature above 100° serve as safety-plugs for boilers and automatic sprinklers. Bis-

muth alloys, melting at a given temperature, are used for tempering steel; the pencils used for writing on the so-called metallic paper likewise consist of an alloy of bismuth.

Bismuth in very small quantities renders gold and silver brittle, and greatly diminishes the conductivity of copper for electricity.

Molten bismuth, to which 0·05 per cent. of tellurium has been added, solidifies to a minutely crystalline mass, entirely different in appearance, fracture, &c., from the pure metal.

When bismuth is treated with sodammonium a compound of the formula $BiNa_3$ is formed as a bluish black mass, which takes fire in the air, and decomposes water with evolution of hydrogen.[1]

COMPOUNDS OF BISMUTH.

Bismuth and Oxygen.

451 These elements unite together to form the following compounds:

Bismuth dioxide,	Bi_2O_2.
Bismuth trioxide,	Bi_2O_3.
Bismuth tetroxide,	Bi_2O_4.
Bismuth pentoxide,	Bi_2O_5.

The dioxide has only very feeble basic properties, whereas the trioxide is a well-marked basic oxide, and corresponds to the stable salts of bismuth of the general formula BiR'_3. The pentoxide, on the other hand, is a very weak acid-forming oxide, the alkali salts of which are decomposed by water.

Bismuth Dioxide, Bi_2O_2, is formed when the metal is heated not quite to its melting-point in the presence of air. It is obtained in a purer state when bismuth trioxide and tin dichloride are added together in molecular proportions, and the mixture dissolved in hydrochloric acid, the acid solution being poured into a tolerably concentrated solution of caustic potash. The brownish-black precipitate thus obtained is treated with concentrated caustic potash in order to separate the stannic acid, and then washed and dried at 100°. It is a greyish-black crystalline

[1] Joannis, *Compt. Rend.* 1892, **114**, 585.

powder which, when heated in the air, burns like tinder.[1] When treated with hydrochloric acid it yields metallic bismuth and bismuth trichloride.

$$3Bi_2O_2 + 12HCl = 4BiCl_3 + 6H_2O + 2Bi.$$

In the process described above for the preparation of the pure dioxide a stannate of the oxide is first formed. This compound can best be obtained by pouring a solution of tin dichloride upon powdered nitrate of bismuth. It is a dark yellow powder.

Bismuth Trioxide, Bi_2O_3, is found as bismuth ochre in Cornwall, Virginia, Siberia, and the Erzgebirge, as a yellow or greenish-grey amorphous mass or as a powder, and it usually contains ferric oxide and other impurities. In order to prepare it artificially, the hydroxide, carbonate, or nitrate is heated. Thus obtained, it is a yellow powder, having a specific gravity of 8·2, which fuses at a red-heat, forming a brown liquid solidifying to a yellow crystalline mass. When a boiling solution of a bismuth salt is precipitated with potash, the trioxide is obtained in microscopic needles, and if this be melted with caustic potash the product is found to crystallise in rhombic prisms. When the oxide is prepared by adding potassium cyanide to bismuth nitrate solution, boiling and heating the resulting grey powder in the air, it crystallises in tetrahedra belonging to the regular system. It is therefore isodimorphous with antimony oxide.[2] The oxide prepared by roasting the metal appears to have been employed as a yellow paint in Agricola's times. Bismuth has also been used for replacing lead in flint-glass or strass, as the glass thus produced possesses a much higher refractive index than ordinary flint-glass; if, at the same time, the potash be replaced by thallium, a glass is obtained whose refractive index is higher than that of any other kind.

Bismuth trioxide is a stronger base than the corresponding oxide of antimony, and forms a well-defined series of salts, which are characterised by the ease with which they are converted by water into insoluble basic salts.

Bismuth Trihydroxide, $Bi(OH)_3$, is obtained as a white amorphous powder by precipitating a bismuth salt with cold caustic soda or ammonia.

Bismuth Tetroxide, $Bi_2O_4 = (BiO)BiO_3$, is formed when the trioxide is fused with alkalis in contact with the air or when it

[1] Schneider, *Pogg. Ann.* 1863, **119**, 331.

[2] Muir and Hutchinson, *Journ. Chem. Soc.* 1889, i. 143.

is treated with caustic potash and chlorine passed in until the mass becomes of a yellowish-red colour. On addition of nitric acid the yellowish-red hydrate is thrown down, $Bi_2O_4 + 2H_2O$.

452 *Bismuth Pentoxide*, Bi_2O_5, is obtained as a brown powder by heating bismuthic acid to 130°. It is an extremely unstable compound and when heated loses oxygen, which gas is also given off on treatment with sulphuric acid, whilst chlorine is evolved when the substance is heated with hydrochloric acid.

Bismuthic Acid, $HBiO_3$, is obtained by passing a current of chlorine into a boiling solution of caustic potash containing bismuth trioxide in suspension. A red powder then separates out which is washed with dilute nitric acid and water. The same substance may be obtained by fusing caustic potash with a basic nitrate of bismuth in contact with the air until the mass has become dark-brown. On cooling, it is lixiviated with boiling water and the residue treated as above.

The acid also appears to be precipitated when an alkaline 3 per cent. solution of hydrogen peroxide is added to a bismuth salt.[1] Bismuthic acid has only very feeble acid properties and it is doubtful whether any definite salts have been isolated, most of those which have been described as formed by the action of strong alkalis on the acid, being mixtures which are decomposed by prolonged washing with water.[2] The salts appear only to be stable in presence of a large excess of alkali.

Bismuth and the Halogens.

453 *Bismuth Trifluoride*, BiF_3, is obtained as a white powder by dissolving the oxide in hydrofluoric acid and evaporating the solution. An oxyfluoride, BiOF, is formed when the acid is completely neutralised by the oxide. The fluoride forms a double salt with ammonium fluoride, BiF_3,NH_4F.[3]

Bismuth Dichloride, $BiCl_2$, is formed when a slow current of chlorine is passed over the fused metal, or when the metal is heated with calomel to 250° or fused with the trichloride. It is

[1] *Ber.* 1887, **20**, 213.

[2] Muir, *Journ. Chem. Soc.* 1887, 77. See also André, *Compt. Rend.* 1891, **113**, 860; 1892, **114**, 359.

[3] Helmholt, *Zeit. anorg. Chem.* 1892, **3**, 115; see also Muir, Hoffmeister and Robes, *Journ. Chem. Soc.* 1881, i. 33.

and formation of the trichloride and an oxychloride $Bi_4Cl_2O_3$ or $2BiCl_2+3Bi_2O_3$. Water decomposes it with formation of metallic bismuth and the oxychloride, BiOCl.

Bismuth Trichloride, $BiCl_3$, was first prepared by Boyle[1] by heating bismuth with corrosive sublimate. It is also formed when the metal is burnt in a stream of chlorine, or when a concentrated solution of the oxide in hydrochloric acid is distilled and the receiver changed after all the water has come over. Bismuth trichloride is a granular white mass, which melts at from 225° to 230°, boils at 435° to 441°, and yields a vapour having the normal specific gravity of 11·35 (Jaquelain). Heated in a current of hydrogen it is reduced to dichloride.[2] It forms a syrupy liquid when dissolved in a small quantity of water, though a larger quantity of water decomposes it, with formation of *bismuth oxychloride*, BiOCl, which is thrown down as a pure white powder, insoluble in water, though readily dissolved in acids. Heated in the air bismuth oxychloride loses chlorine and takes up oxygen, but in absence of air it becomes yellow-coloured and fuses without decomposition.

When a solution of the oxide in an excess of hydrochloric acid is evaporated, fine needle-shaped crystals are deposited, having the composition $BiCl_3,2HCl$, whilst at 0° a saturated solution of the two deposits crystals of the compound $2BiCl_3,HCl+3H_2O$, which are stable at the ordinary temperature.[3] Bismuth trichloride forms double salts with the chlorides of the alkali metals,[4] and when the anhydrous chloride is treated with ammonia, three distinct compounds are obtained. One of these is a white, very volatile mass, having the formula $BiCl_3+3NH_3$; the two others remain behind in the retort in the process of preparation and have the composition $BiCl_3+2NH_3$ and $2BiCl_3+NH_3$. The first of these forms a dirty-grey mass, whilst the second is red and crystalline. They combine with hydrochloric acid to form double salts, which are also obtained when sal-ammoniac is added to the solution of bismuth in the right proportion and the mixture evaporated.[5] When the dichloride is treated with chlorine a brownish-red powder is obtained of a black, crystalline, slightly volatile mass, which on heating in

[1] *Experiments and Considerations Touching Colours.*

[2] Muir, *Journ. Chem. Soc.* 1876, i. 144.

[3] Engel, *Compt. Rend.* 1888, **106**, 1797.

[4] See Brigham, *Amer. Chem. Journ.* 1892, **14**, 164; and Field, *Journ. Chem. Soc.* 1893, **1**, 546.

[5] Dehérain, *Compt. Rend.* 1862, **54**, 924.

the air decomposes with separation of a portion of the metal, Bi_3Cl_8; this decomposes on heating into chlorine, trichloride, and dichloride.

Bismuth trichloride also combines with nitric oxide [1] to form the yellow compound $2BiCl_3,NO$ and with nitrosyl chloride [2] to form an orange coloured powder $BiCl_3$, NOCl.

Bismuth Tribromide, $BiBr_3$.—When bromine vapour is passed over powdered bismuth an energetic reaction takes place and a red liquid volatilises. This cools to a golden-yellow glistening deliquescent crystalline mass, which melts at 210° and boils at 453°. Bismuth tribromide crystallises from ether in prisms, and water decomposes it into the white insoluble oxybromide, BiOBr. It forms crystalline double salts, with the bromides of the alkali-metals, and with ammonia it forms compounds similar to those of the chloride.

If the tribromide be fused with bismuth a mass of brown crystalline needles is obtained, which probably consists of the *dibromide*. This is decomposed by hydrochloric acid with separation of spongy bismuth.

Bismuth Tri-iodide, BiI_3, is obtained by treating the powdered metal with iodine, and heating the product, or by precipitating a bismuth salt with potassium iodide solution, dissolving in hydriodic acid and reprecipitating with water. It sublimes in greyish-black metallic glistening tablets, which are not decomposed by cold water, though they are converted by hot water into an insoluble oxyiodide. If a solution of the iodide in hydriodic acid be evaporated, rhombic pyramids of $BiI_3+HI+4H_2O$ are deposited. Bismuth iodide forms a large number of double salts, which have been investigated by Nicklés [3] and Linau.[4]

Bismuth Oxyiodide, BiOI, is obtained by decomposition of the tri-iodide with boiling water or by heating the same in the air, as a copper-red crystalline mass, which can be sublimed when heated in the absence of air, but is gradually converted in presence of air into a crystalline oxide

[1] Thomas, *Compt. Rend.* 1895, **121**, 128.
[2] Sudborough, *Journ. Chem. Soc.* 1891, **1**, 662.
[3] *Compt. Rend.* 1860, **50**, 872, and *Journ. Pharm.* [3], **39**, 116.
[4] *Pogg. Ann.* 1860, **111**, 240.

Bismuth and the Elements of the Sulphur Group.

454 *Bismuth Disulphide*, Bi_2S_2, is obtained as a grey metallic lustrous mass of needle-shaped crystals when the two elements are fused together in the proportion of their atomic weights and the mixture allowed to cool quickly. When a current of sulphuretted hydrogen is passed through a dilute alkaline solution of bismuth nitrate free from air, mixed with tin dichloride, the dioxide which is first formed is converted into a black powder having the composition $Bi_2S_2 + 2H_2O$, which on trituration assumes a metallic lustre, and when this is treated with hydrochloric acid the following reaction takes place :—

$$3Bi_2S_2 + 12HCl = 2Bi + 4BiCl_3 + 6H_2S,$$

the bismuth separating out as a spongy mass.

Bismuth Trisulphide, Bi_2S_3, occurs as bismuthite in rhombic crystals, and also massive with a foliated or fibrous structure and having a specific gravity of 6·4. It is found at Brandy Gill, Carrock Fells in Cumberland, at Redruth and Botallack, and other localities in Cornwall, in the Erzgebirge, in Bolivia, and in other localities. It is obtained artificially by fusing the metal with an excess of sulphur, or by precipitating a solution of bismuth chloride with sulphuretted hydrogen. Thus prepared it forms a blackish-brown precipitate easily soluble in nitric acid and in boiling concentrated hydrochloric acid, but not in alkalis or their sulphides. When it is heated to 200° in a solution of the latter it becomes crystalline, assuming the form of bismuthite.

The amorphous sulphide dissolves in potassium sulphide solution and very sparingly in sodium sulphide solution,[1] and forms salts of the formula Bi_2S_3,K_2S and Bi_2S_3,Na_2S, when it is fused with sulphur and an alkali carbonate.[2]

Bismuth Oxysulphides.—The compound Bi_4O_3S, occurs as karelilinite, in a crystalline mass having a strongly metallic lustre and found at the Savodinck Mine in the Altai. If a mixture of 40 parts of sulphur and 142 parts of bismuth trioxide be heated to dark redness, a grey crystalline mass of $Bi_6O_3S_4$ is formed.

The oxysulphide, Bi_2O_3S, is formed by the action of sulphuretted hydrogen on bismuth pentoxide suspended in boiling benzene.[3]

[1] Ditte, *Compt. Rend.* 1895, **120**, 186.
[2] Schneider, *Pogg. Ann.* 1869, **136**, 460.
[3] Scherpenberg, *Journ. Chem. Soc.* 1890, ii. 216.

Bismuth Chlorosulphide, BiSCl, is obtained by fusing together in the air 1 part of sulphur and 8 parts of ammonium bismuth chloride, or by heating the latter compound in a current of sulphuretted hydrogen (Schneider), and is also formed when the chloride is heated in dry sulphuretted hydrogen or the sulphide in dry chlorine. It is a reddish brown solid and is not decomposed by water. The corresponding *sulphobromide* is obtained in a similar manner, whereas the *sulphiodide* can only be prepared by heating bismuth iodide with the trisulphide. All three compounds are decomposed by sulphuretted hydrogen at a bright red heat.[1]

Bismuth Trisulphate, $Bi_2(SO_4)_3$, is obtained as an amorphous white mass by dissolving the metal or the sulphide in concentrated sulphuric acid and evaporating. This salt is decomposed by water with formation of the basic salt, Bi_2O_3,SO_3+2H_2O. When this is heated it loses water, and on cooling a yellow mass, consisting of Bi_2O_3,SO_3 is obtained. This salt is also obtained by heating the other sulphates. Another of these basic salts has the composition $Bi_2O_3,2SO_3+3H_2O$, and is obtained in small needles by acting upon the nitrate with sulphuric acid. Several other basic salts have also been described.

455 *Bismuth Triselenide*, Bi_2Se_3, is obtained by fusing the elements together as a metallic lustrous brittle crystalline mass, having a specific gravity of 6·82, and which is attacked only by nitric acid and aqua regia.

Bismuth Tritelluride, Bi_2Te_3, occurs as tetradymite in metallic pale steel-grey rhombohedra, or in foliated or granular masses having a specific gravity of 7·2 to 7·9. It is found in Transylvania, Hungary, Sweden, Norway, and in several localities in the United States, together with other tellurium ores. In some varieties of this mineral a portion of the tellurium is replaced by sulphur and selenium, although the analyses of the pure material correspond to the above formula. G. Rose and P. Groth[2] consider this mineral to be an isomorphous mixture of the elements, as it is not isomorphous with bismuthite, and as bismuth and tellurium can be fused together in all proportions.

[1] Muir and Eagles, *Journ. Chem. Soc.* 1895, **1**, 90.

[2] *Tabell. Uebersicht. d. Einf. Mineralien*, 73.

Bismuth and the Elements of the Nitrogen Group.

456 *Bismuth Trinitrate*, $Bi(NO_3)_3+3H_2O$, is obtained in large transparent asymmetric prisms by dissolving the metal in nitric acid and evaporating the solution, which corrodes paper, and must, therefore, be filtered through asbestos or pounded glass. The crystals, which are deliquescent, are decomposed on heating, first losing their water, and then leaving a residue, first of basic salt, and lastly of the trioxide.

Basic Bismuth Nitrate, $Bi(OH)_2NO_3$.—Libavius was aware that the solution of bismuth in nitric acid is precipitated by water, and Lemery, who describes the preparation of this compound, states that water containing common salt should be employed for this precipitation, pure water precipitating it, but much more slowly; and he adds that the product obtained weighs more than the metal employed. The reason of this, he explains, is that a certain quantity of spirit of nitre remains behind, even if the precipitate be well washed. Boyle states that the solution of bismuth in aqua-fortis is almost completely precipitated by common water. In spite of this many chemists, looking at the analogy between lead and bismuth, believed that salt water was necessary for the precipitation; indeed the substance was for some time termed horn-bismuth. This error was definitely rectified by Pott, in 1739.

Basic nitrate of bismuth, formerly termed *magistery of bismuth*, is used as an important medicine, and many different receipts are given for its preparation. According to the British Pharmacopœia, *bismuth subnitras* is best obtained by dissolving 2 parts by weight of bismuth in a mixture of 4 parts of nitric acid of specific gravity 1·42, diluted with three parts of water. The clear liquid is poured off from any insoluble matter, and evaporated to the point at which it occupies two volumes, and this is then poured into 80 parts of distilled water. The clear liquid is then decanted, and diluted with water; this is well stirred up, and the precipitate collected on a filter and dried at a temperature not higher than 55°. The German and French pharmacopœias recommend somewhat similar processes. In all these methods a considerable quantity of bismuth remains in solution, and this may be obtained, as the hydroxide, by precipitating with ammonia.

Basic bismuth nitrate is a crystalline powder which reddens

moistened litmus paper. Its composition varies somewhat, according to the quantity of water used in the preparation, and a large number of basic salts have been described. When washed for a long time it becomes more basic, until at last the hydroxide is formed.

Basic nitrate of bismuth is largely used as a medicine in cases of chronic diarrhœa and cholera. The amount of this material employed in the French army amounts to 1,250 kilos per annum, most of which goes to Algiers. During the American war it was largely used in the field-hospitals for similar purposes, and its consumption in Germany is also large. It is moreover used in considerable quantities as a cosmetic; and this use of basic nitrate of bismuth is due to Lemery, who recommends it for softening the skin. When used for this purpose it was first termed *blanc d'Espagne*, which name, however, was used to designate many other white pigments. Another name for this cosmetic is *blanc de fard*.

The basic nitrate as well as the oxide is also used for giving a colourless iridescent glaze to porcelain. This is obtained by rubbing up basic nitrate with resin, and gently heating the mixture with lavender oil. It can be coloured by the addition of oxides, such as oxide of chromium, which gives to it a sulphur or lemon-yellow colour. With addition of 5 per cent. of gold to the oxide of bismuth, a splendid copper-red colour with a reflected golden lustre is obtained. When a smaller quantity of this same substance is employed, the glass assumes a violet or pure blue colour, whilst with another treatment a rose-red tint is obtained. These glazes are also used in glass-staining.

457 *Bismuth Orthophosphate*, $BiPO_4$, is precipitated when solutions of bismuth nitrate and phosphoric acid are brought together in presence of nitric acid. In the same way an insoluble *pyrophosphate*, $Bi_4(P_2O_7)_3$, is prepared with pyrophosphoric acid. When the oxide and phosphorus pentoxide are fused together a clear glass is obtained, which on slow cooling becomes crystalline, and probably consists of the tetrametaphosphate.

Bismuth Arsenate, $Bi_4(As_2O_7)_3$, is a white precipitate insoluble in water and nitric acid but soluble in hydrochloric acid.

Phosphorus and *arsenic* do not readily combine with bismuth. The first of these forms a compound with molten bismuth, and if a current of phosphuretted hydrogen be passed through a solution of bismuth, a black phosphide is precipitated, which,

however, decomposes in absence of air into its elements. An alloy of bismuth and arsenic gives up the whole of the latter when heated. Arseniuretted hydrogen produces a black precipitate in bismuth solutions which behaves in a precisely similar way.

Bismuth and the Elements of the Carbon Group.

458 *Basic Bismuth Carbonate*, $2(BiO)_2CO_3+H_2O$, is obtained as a white precipitate when ammonium carbonate is poured into a solution of bismuth nitrate and dried at a gentle heat. It is employed as a medicine. At 100° it loses water, and when more strongly heated is readily converted into the trioxide.

The mineral bismutite is another basic carbonate, $3(BiO)_2CO_3+2Bi(OH)_3+3H_2O$. This is found at Schneeberg, at Chesterfield, South Carolina, and at other places, together with bismuth ores. It is a white or siskin-green earthy mass and sometimes occurs in acicular pseudomorphous crystals.

Bismuth Silicate, $Bi_4(SiO_4)_3$, occurs as eulytine, found in small glistening yellow or brown regular tetrahedra and occurring in the Erzgebirge together with phosphates of iron and manganese.

Detection and Estimation of Bismuth.

459 When a bismuth compound is heated in the upper reduction-flame of the Bunsen burner on an asbestos thread, a cold porcelain dish, held above it, receives a brown or black deposit of metallic bismuth, which is only slowly dissolved in cold dilute nitric acid. A brittle metallic bead is obtained when the compound is heated on the carbonised match, and this dissolves in nitric acid, yielding a brown precipitate of bismuth dioxide with stannous chloride and caustic soda. A characteristic reaction of the bismuth salts is the precipitation of the blackish-brown sulphide with sulphuretted hydrogen, insoluble in sulphide of ammonium, and easily soluble in nitric acid. In addition to this, water produces, in solutions which are not too strongly acid, a white precipitate of an insoluble basic salt, and ammonia throws down a white precipitate of the hydroxide insoluble in excess. These reactions serve to separate bismuth from other metals, as well as to detect its presence. If other metals precipitable by sulphuretted hydrogen be present, the

washed precipitate is first digested with sulphide of ammonium, in order to separate arsenic, antimony, and tin. The precipitate is then well washed, dissolved in nitric acid, and dilute sulphuric acid added to the filtrate to separate lead; the precipitate is filtered off, and an excess of ammonia added which throws down the bismuth as the hydroxide, whilst any copper or cadmium present remains in solution. The precipitate is dissolved in a small quantity of hydrochloric acid, the liquid concentrated by evaporation, and added to a large quantity of water, when the insoluble oxychloride is precipitated. Care, however, must be taken that the whole of the antimony is previously removed by a long digestion of the sulphides with sulphide of ammonium, and the residue well washed with water, for otherwise an insoluble oxychloride of antimony may be precipitated, and this may be mistaken for bismuth.

Bismuth can be determined *quantitatively* in several ways. If the solution consists only of nitrate, it may be precipitated with ammonium carbonate, heated for some time almost to boiling, filtered, the precipitate dried and converted by ignition into the trioxide which is weighed. If other acids are present, the bismuth is precipitated by sulphuretted hydrogen, the washed precipitate dissolved in nitric acid and treated as above; or it may be dried, any excess of sulphur got rid of by carbon bisulphide, and the residual pure sulphide dried at 100° and weighed. Bismuth may also be estimated as the metal by reduction with potassium cyanide. The metallic mass is well washed with water and alcohol, and weighed after drying. Lastly, if the solution of the nitrate contains only a small quantity of free acid, it may be precipitated with potassium dichromate, or with arsenic acid, and the precipitate dried and weighed.

The atomic weight of bismuth has been determined by several chemists, but without very concordant results. In 1851 Schneider[1] by converting the metal into the oxide obtained the number 206·5, and this was confirmed in 1883 by Löwe,[2] who used the same method and obtained the number 206·3, and by Marignac,[3] who, in 1883, found the atomic weight to be 206·7 by converting the oxide into the sulphate. Dumas,[4] on the other hand, in 1859, by the analysis of the chloride obtained the number 208·6, which is certainly too high. In 1890, Classen[5]

[1] *Pogg. Ann.* 1851, **82**, 303.
[2] *Fres. Zeitsch.* 1883, 498.
[3] *Fres. Zeitsch.* 1884, 120.
[4] *Ann. Chim. Phys.* 1859 [3], **55**, 177.
[5] *Ber.* 1890, **23**, 938.

made a series of nine concordant experiments in which carefully purified bismuth was converted into the oxide and found the number 207·3. Finally Schneider,[1] in 1894, repeated his experiments and again obtained the number 206·5. Until further experiments are made the number 207 may be taken as representing the atomic weight (O = 15·88).

GROUP VI.

Sub-Group (a). Oxygen and the Sulphur Group.

Oxygen.
Sulphur.
Selenium.
Tellurium.

Sub-Group (b). The Chromium Group.

Chromium.
Molybdenum.
Tungsten.
Uranium.

460 In this group, as in Groups I, II, and III, the elements may be divided into two well-defined sub-groups, as shown in the above table, the sub-group (a) consisting of non-metallic elements, while those in the sub-group (b) are metals. In the strict periodic classification oxygen falls in the even series, and therefore belongs to the chromium sub-group, but as in the case of beryllium in Group II, it is much more nearly allied to the members of the odd series.

Oxygen is gaseous at the ordinary temperature, whilst sulphur, selenium and tellurium are solids, the melting and boiling points of which increase with increasing atomic weight. The elements of the chromium group are only fusible at very high temperatures, and are only reduced from their oxides with great difficulty.

All the metals unite with the elements of the oxygen group to form oxides, sulphides, selenides and tellurides; and the different series of compounds thus formed present strong analogies among themselves, as has already been seen in the

[1] *J. pr. Chem.* 1894 [2], **50**, 461.

description of the compounds of the metals of the previous groups. The analogy which exists between the "oxy-salts" obtained by the union of a basic and acidic oxide, and the "thio-salts" formed in a similar manner from the acidic and basic sulphides, has also been frequently alluded to.

The most characteristic compounds formed by these elements (with, of course, the exception of oxygen) are the trioxides and their numerous derivatives. All of these behave as acid-forming oxides, and give rise to well-defined series of compounds having the general formula, $M'_2M^{vi}O_4$, in which M′ represents hydrogen, or a monovalent metal, and M^{vi} an element of the group under consideration. These possess strongly marked analogies with each other, and the salts of the same metal are as a rule isomorphous. These oxides also form salts containing from two to eight equivalents of the acidic oxide to one of basic oxide, such as the disulphates $M'_2O{\cdot}2SO_3$, and dichromates, $M'_2O{\cdot}2CrO_3$, the trichromates $M'_2O{\cdot}3CrO_3$, the octotungstates, $M'_2O{,}8WO_3$, etc.

The constitution of the normal acids corresponding to the trioxides is represented by the formula $O_2M^{vi}\langle^{OH}_{OH}$, and the hydroxyl groups in these acids may be replaced by negative radicals such as the halogens. The compounds thus formed from the elements of lower atomic weight, such as sulphur and chromium, are acidic chlorides, and are at once decomposed by water with formation of the acid; but as the atomic weight of the element increases, the basicity of the radical $M^{vi}O_2$ also increases, and the compounds become more stable, until in the case of uranium, the compounds formed by negative radicals with the group UO_2 are the most stable series of salts of that metal.

The elements of this group also form other oxides containing a less amount of oxygen than the trioxide; in the case of sulphur, selenium, and tellurium, these oxides (RO_2) are acidic or neutral, whilst with the metals of the chromium group (R_2O_3 and RO_2) they are usually basic, and give rise to series of salts which often have strong reducing properties, owing to their tendency to unite with oxygen forming derivatives of the trioxide.

The elements of sub-group (a) combine with hydrogen and the alkyl radicals forming volatile compounds, but no similar derivatives have been obtained from the elements of sub-group (b).

Oxygen is divalent in almost all of its compounds, but pos-

sibly sometimes acts as a tetrad. The remaining elements are, as stated above, hexavalent in their most characteristic oxygen compounds, but the valency in their other compounds varies very considerably; the elements sulphur, selenium, and tellurium, are always divalent towards hydrogen and the alkyl radicals, and usually either di-, tetra- or hexavalent in their other compounds, but no such regularity is observed in sub-group (b).

The compounds of oxygen, sulphur, selenium and tellurium have already been described in Vol. I (pp. 214—446).

CHROMIUM, Cr = 51·7

461 In 1762 Lehmann, in a letter to Buffon, "de nova mineræ plumbi specie crystalline rubra," described a new mineral from Siberia, now termed crocoisite or lead chromate. Vauquelin and Macquart investigated the composition of this mineral in 1789, and came to the conclusion that it contained lead, iron, alumina, and a large quantity of oxygen. However, when the former chemist re-investigated the subject in 1797, he found that the lead present was combined with a peculiar acid, which he recognised as the oxide of a new metal. To this the name of *chromium* was given, because its compounds are usually coloured, (from χρῶμα, colour). The discovery of this new metal in crocoisite was also made simultaneously and independently by Klaproth.

Chromium is not a very common substance, and does not occur in the free state. It is found in several other minerals besides crocoisite or lead chromate, $PbCrO_4$, especially as chrome-iron-stone or chromite, $FeO.Cr_2O_3$, a mineral which is the chief ore of chromium and is the one usually employed for the manufacture of the chromium compounds. Chromium also forms the colouring matter of several minerals; thus the green colour of emerald, as was shown by Vauquelin, is due to chromium; whilst serpentine, penninite, chromic mica or fuchsite, and other minerals owe their colour to the same metal.

Metallic chromium is obtained by the reduction of the oxide or chloride; thus Deville obtained it by strongly heating the oxide and sugar charcoal in a lime crucible,[1] and Wöhler by heating chromic chloride with zinc under a layer of sodium

[1] *Compt. Rend.* 1857, **44**, 673.

chloride, and treating the alloy of zinc and chromium thus obtained with nitric acid;[1] it then forms a grey powder consisting of minute octohedra.[2] Jäger and Krüss obtained the pure metal by this process in tin-white rhombohedra.[3] Magnesium and sodium have also been employed in place of metallic zinc, the first of these being specially suitable for a laboratory preparation. The best method of preparation is however that of Moissan,[4] which consists in heating a mixture of chromium sesquioxide and carbon in the electric furnace; the first product contains large quantities of carbon, which is removed by first heating strongly with lime, when the greater part of the carbon is converted into calcium carbide, and the remainder is eliminated by fusing the purified product in a crucible brasqued with the double oxide of calcium and chromium.

Pure chromium is somewhat harder than glass, and has a melting point considerably higher than that of platinum, whilst if it contains 1·5—3 per cent. of carbon it melts at a lower temperature, but can only be cut by the diamond. The polished metal resembles iron, but is brighter and has a somewhat whiter colour: it has a specific gravity of 6·92 at 20°, a specific heat of 0·1216, and burns when heated in the oxyhydrogen flame more brilliantly than iron. It is attacked slowly in the cold and rapidly on heating by dilute hydrochloric acid, and also dissolves slowly in dilute sulphuric and nitric acids. With concentrated sulphuric acid it evolves sulphur dioxide, with formation of a deep-coloured solution, but it is unaffected by hot concentrated nitric acid.

Chromium combines with silicon and boron at the temperature of the electric furnace, yielding a crystalline boride and silicide, both of which are extremely hard.

462 *Chromium Amalgams.*—When a strong hydrochloric acid solution of chromic chloride is electrolysed with a powerful current using a mercury cathode and a platinum anode, a solid chromium amalgam is obtained, having the composition Hg_3Cr. Under a pressure of 200 kilos to the square cm. this loses mercury, yielding an amalgam of the composition HgCr. When either of these amalgams is heated in a vacuum at 300°,

[1] *Annalen*, 1859, **111**, 230.
[2] Prinz, *Compt. Rend.* 1893, **116**, 392.
[3] *Ber.* 1889, **22**, 2052.
[4] *Compt. Rend.* 1893, **116**, 349; 1894, **119**, 185.

the whole of the mercury is driven off, leaving the chromium as a powder, which is pyrophoric at the ordinary temperature, and also combines with nitrogen on heating.[1]

COMPOUNDS OF CHROMIUM

Chromium and Oxygen.

463 Chromium combines with oxygen to form two well-defined oxides, viz., chromium sesquioxide, Cr_2O_3, and chromium trioxide, CrO_3. The former is a basic oxide, corresponding to the chief series of chromium salts, in which the metal is trivalent; whilst the latter is an acidic oxide, which combines with water to form chromic acid, H_2CrO_4, the salts of which resemble the corresponding sulphates, selenates and tellurates, with which they are frequently isomorphous.

Chromium monoxide, CrO, is unknown, but the corresponding hydroxide has been prepared, and yields with acids the *chromous* salts, in which the metal is divalent. A number of other oxides have been described which may be regarded as formed by the combination of one or other of the basic oxides with the acidic trioxide; the best defined of these is that frequently termed chromium dioxide, which has really the constitution $Cr_2O_3.CrO_3 = 3CrO_2$, and will be described with the other chromates.

464 *Chromous Hydroxide*, $Cr(OH)_2$, is formed by the action of aqueous potash freed from air on chromous chloride solution, as a brownish yellow precipitate, which is readily oxidised with evolution of hydrogen, and on drying in absence of air has a dark brown colour. On ignition it yields water, hydrogen and chromic oxide:

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$

Chromium Sesquioxide, or *Chromic Oxide*, Cr_2O_3, occurs in the hydrated form as chrome ochre, and is obtained artificially as a dull green amorphous powder by igniting the hydroxide, or by heating a mixture of potassium dichromate with sulphur or sal-ammoniac and lixiviating the residue. The colour of the oxide prepared by gently igniting mercurous chromate, Hg_2CrO_4, in a covered crucible is a very fine green. It melts at the temperature of the oxyhydrogen blowpipe, solidifying to a crystal-

[1] Ferée, *Compt. Rend.* 1895, **121**, 822.

line almost black mass. Chromic oxide is also obtained in the crystalline state by fusing the amorphous substance with calcium carbonate and boron trioxide, or by ignition in a stream of oxygen. Wöhler's[1] method of preparing crystalline chromic oxide consists in passing the vapour of chromyl chloride, CrO_2Cl_2, through a red-hot tube, when chromic oxide is deposited in dark-green, lustrous, very hard, hexagonal crystals, which have a specific gravity of 5·21. Another method consists in heating potassium dichromate either alone or mixed with common salt; the ignited mass is dissolved in water, when chromic oxide remains in bright iridescent spangles, which have a specific gravity of 5·01.[2]

The strongly ignited oxide is almost insoluble in acids, and in order to bring it into solution it must either be heated for a length of time with strong sulphuric acid or fused with acid potassium sulphate. Chromic oxide is used in the preparation of coloured glass, enamels, and porcelain, imparting to them a fine green tint. It is also used in ordinary painting, forming one of the most permanent greens, known as chrome-green.

Chromic Hydroxides.—Several modifications of chromic hydroxide are known; the first, which reacts directly with three equivalents of acid forming the normal chromic salts, is obtained by the action of alkalis on cold solutions of violet chromic salts, and has probably the constitution $Cr(OH)_3$. It is best prepared by adding ammonia to a solution of a violet chromic salt free from alkali, and forms a pale blue precipitate, which after drying over sulphuric acid has the composition $Cr(OH)_3 + 2H_2O$. When heated in a current of hydrogen at 200° it yields the hydroxide CrO(OH), which occurs mixed with clay as chrome ochre or wolchonskoïte; at a red heat this commences to glow strongly and passes into chromic oxide. Another hydroxide, which has probably the constitution $Cr_2O(OH)_4$, is obtained by dissolving the first named hydroxide in caustic soda and reprecipitating by hydrochloric acid, and is also formed by the action of alkalis on the green chromic salts of oxy-acids (p. 841); when treated with acids it only reacts with two equivalents of the latter, yielding the above green salts, which however on standing with acid gradually combine with it, forming the normal violet salts. Another hydroxide which also reacts with only two equivalents of acid is obtained, according to Recoura, by the action of alkalis on the chromic oxychloride obtained by oxida-

[1] *Annalen*, 1846, **60**, 203.

[2] Schröder, *Pogg. Ann.* 1859, **106**, 226; **107**, 113.

tion of chromous chloride solution. It differs from the foregoing in the amount of heat evolved by the action of two equivalents of acid.[1]

Guignet's Green is obtained by fusing together potassium dichromate and crystallised boric acid in equal molecular proportions and lixiviating the fused mass with water. The residue after grinding is a fine green powder, and is largely used as a pigment. It is usually described as having the composition $Cr_2O(OH)_4$, but it always contains boric acid, and may possibly have the composition $3Cr_2O_3,B_2O_3+4H_2O$.

Colloidal Chromic Hydroxide.—Freshly precipitated and washed chromic hydroxide dissolves in chromic chloride, and on dialysing this solution Graham obtained a liquid containing 33 molecules of Cr_2O_3 to one of HCl. The deep dark green solution does not undergo change on boiling or dilution, but at once coagulates on addition of the smallest quantity of a salt.[2] The precipitated colloid has no constant composition between 15° and 280°.[3]

Chromites.—Like alumina, chromic oxide acts as an acidic oxide towards strong bases, yielding salts termed the chromites. Thus a green compound of chromic oxide with an alkali is thrown down on the addition of potash or soda to a solution of a chromic salt, and the alkali cannot be removed even by boiling water. This precipitate is, however, easily soluble in an excess of the precipitant, but can be again thrown down either by partial neutralisation with acids or by boiling the solution. When caustic soda is added to a solution of a chromic salt and a salt of magnesium a precipitate is obtained of a compound of magnesia and chromic oxide which does not dissolve in an excess of alkali.

The chromites may also be obtained by the action of boiling aqueous alkalis on the corresponding sulphochromites (p. 846).

Zinc Chromite, $ZnCr_2O_4$, is obtained by fusing the two oxides with boron trioxide at a white heat, when blackish-green octohedra having a specific gravity of 5·309 are obtained.

Manganese Chromite, $MnCr_2O_4$, is obtained in a similar way, and forms very hard iron-grey octohedra, which have a specific gravity of 4·87.

Ferrous Chromite, $FeCr_2O_4$.—This occurs in nature as chromite or chrome-iron-ore. It is rarely found crystallised in regular

[1] *Ann. Chim. Phys.* 1887 (6), **10**, 60.
[2] Graham, *Phil. Trans.* 1861, 183.
[3] van Bemmelen, *Rec. Trav. Chim.* 1887, **7**, 114.

octohedra, generally occurring massive, with a granular crystalline fracture. Alumina and magnesia occur frequently as isomorphous constituents, and in some cases chromite contains more iron than corresponds to the above formula, the composition approximating to $Fe_2Cr_2O_5 + Fe_3Cr_4O_9$.[1] Chrome-iron ore is found in the Shetland Islands, Norway, the United States, Hungary, Greece, Asia Minor, in the Urals, and in New Caledonia.

Chromium Trioxide, Chromic Acid, and the Chromates.

465 When chromic oxide is heated to redness with an alkali in presence of air or with addition of an oxidising agent such as nitre, potassium chlorate, &c., a yellow soluble mass is obtained, consisting of an alkali chromate. The chromates are also formed when an alkaline solution of chromic oxide is treated with lead peroxide, potassium permanganate, chlorine, bromine, hypochlorites or other oxidising agents:

$$Cr_2O_3 + 10KOH + 3Br_2 = 2K_2CrO_4 + 6KBr + 5H_2O.$$

The chromates usually possess a yellow, yellowish-red, or red colour. Besides the normal salts we are acquainted with basic salts, but not with any acid salts. The salts frequently termed acid salts are dichromates corresponding to the disulphates, and are salts of dichromic acid, $H_2Cr_2O_7$ (p. 829). Of these the most important is common red potassium dichromate, $K_2Cr_2O_7 = K_2CrO_4 + CrO_3$. We are also acquainted with trichromates and other polychromates.

Chromium Tricxide or *Chromic Anhydride*, CrO_3.—This compound is formed by the action of strong sulphuric acid on solutions of the chromates. According to Zettnow[2] the best yield is obtained when 300 grams of potassium dichromate are mixed with 500 cc. of water, 420 cc. of concentrated sulphuric acid added, and the mixture allowed to stand for twelve hours in order that the acid potassium sulphate may crystallise out. The mother-liquor is then heated to from 80° to 90°, and 150 cc. of sulphuric acid added together with enough water to dissolve the crystals of trioxide which at first separate out. After standing for twelve hours the liquid is poured off from the crystals which have separated, and a second and a third

[1] Christomanos, *Ber.* 1877, **10**, 343. [2] *Pogg. Ann.* 1871, **143**, 471.

crop may be obtained by concentration. The liquid is drained off from the crystals, and these are then washed on a pumice-stone or asbestos filter by the aid of a filter pump with pure nitric acid, having a specific gravity of 1·46, the adhering nitric acid being removed by passing a current of dry air over the crystals heated in a tube from 60° to 80°.[1]

Chromium trioxide may also be obtained by the action of an excess of nitric acid of sp. gr. 1·38 on barium chromate, the barium nitrate being separated by crystallisation.[2]

Chromium trioxide exists either as a red woolly mass or as long scarlet rhombic prisms having a strong lustre, has a specific gravity of 2·78, and melts at 193° to a dark-red liquid, which solidifies to a reddish-black crystalline mass, having a metallic appearance. At 250° it is resolved into oxygen and the sesquioxide.

Chromium trioxide is easily converted into chromic oxide by reducing agents, such as sulphur dioxide, hydrogen sulphide, stannous chloride, arsenious oxide, ferrous salts, zinc, &c., and many organic compounds also act in the same way. Thus if strong alcohol be dropped on to the dry trioxide reduction takes place with incandescence, and if the trioxide be previously mixed with a little powdered camphor, the chromic oxide formed assumes the appearance of a green mossy vegetation. Paper, sugar, oxalic acid, &c., also reduce the solution of the trioxide, especially on warming. When the trioxide is heated with hydrochloric acid, chlorine is liberated, and when heated with sulphuric acid it decomposes with evolution of oxygen. The aqueous solution of chromium trioxide as well as its solution in glacial acetic acid is often used in organic chemistry as an oxidising agent. Still more commonly a mixture of potassium dichromate and dilute sulphuric acid is employed for this purpose, in which case chrome-alum is obtained as a by-product. Chromium trioxide dissolves without alteration in cold dilute alcohol and in pure ether, and it is also soluble in concentrated sulphuric acid, but not in an acid containing from 16 to 17 per cent. of water. It deliquesces on exposure to air, forming a brown solution which on dilution with water becomes of a yellowish-red colour. This dyes the skin as well as silk and wool of a yellow colour, and possesses an acid and astringent taste.

[1] Bunsen, *Annalen*, 1868, **148**, 290.
[2] Duvillier, *Compt. Rend.* 1867, **65**, 711.

466 *Chromic Acid*, H_2CrO_4, is obtained by warming the trioxide for some time with a quantity of water insufficient for its complete solution, and decanting the clear liquid. The acid separates out on cooling in rose red crystals which are stable over sulphuric acid but readily yield the trioxide and water on warming.[1] From the high conductivity of the solutions of chromic acid Ostwald concludes that the dissolved acid is present as dichromic acid, $H_2Cr_2O_7$.[2]

Chromic acid in its chemical properties resembles sulphuric acid, and the normal salts are usually isomorphous with the corresponding sulphates. The constitution of chromic acid is represented by the formula $CrO_2(OH)_2$ and the hydroxyl groups may be replaced by halogens and other radicals, such as the amido-group, giving rise to substances analogous to those derived in a similar manner from sulphuric acid. In the same way dichromic acid and the dichromates correspond to disulphuric acid and the disulphates; thus the former have the constitution represented by the formula $(OH)CrO_2{-}O{-}CrO_2(OH)$, and the hydroxyl groups in these compounds may also be replaced by other simple or compound radicals. In addition, salts are also known containing three and four molecules of chromium trioxide to one molecule of basic oxide, which are known as the trichromates and tetrachromates, and whose constitution is represented by the formulæ:

$M'O{-}CrO_2{-}O{-}CrO_2{-}O{-}CrO_2{-}OM'$

$M'O{-}CrO_2{-}O{-}CrO_2{-}O{-}CrO_2{-}O{-}CrO_2{-}OM'$

Normal or *Yellow Potassium Chromate*, K_2CrO_4, is obtained by the addition of potash to a solution of the dichromate. On

[1] Moissan, *Compt. Rend.* 1884, **98**, 1581.
[2] *Zeit. physikal. Chem.* 1888, **2**, 78.

evaporating the solution yellow rhombic pyramids crystallise out, which are isomorphous with potassium sulphate, and crystallise with the latter salt in all proportions. It has a specific gravity of 2·71 at 3·9°, and does not undergo alteration in the air. On heating, it becomes red-coloured and melts at a high temperature without decomposition, solidifying on cooling to a crystalline mass. It dissolves in water with a yellow colour which is perceptible even when very small quantities of the substance are present, one part of the salt imparting a distinct yellow tint to 400,000 parts of water. One hundred parts of water dissolve:

At	0°	20°	60°	100°
K_2CrO_4	58·90	62·94	71·02	79·10 parts.

The saturated solution boils at 104·2° under 718 mm. pressure. The salt has a bitter cooling taste and an alkaline reaction. On evaporating its solution red crystals of the dichromate are first deposited and afterwards the yellow crystals of the neutral salt. It is decomposed by all acids, even by carbonic acid with formation of the dichromate. It is insoluble in alcohol.

Potassium Dichromate, or *Bichromate of Potash*, $K_2Cr_2O_7$, serves as the point of departure for the preparation of almost all the other chromium compounds, and is prepared on the large scale from chrome-iron ore.

Up to the year 1820, potassium dichromate was used only for the purpose of making chrome-yellow, and was prepared by the calcination of chrome-iron ore with costly saltpetre. In the above year Köchlin introduced potassium dichromate into the process of Turkey-red dyeing, and it was soon employed for a variety of other purposes, especially in wool-dyeing. In its preparation potashes were employed instead of saltpetre, and the chrome-iron stone was oxidised in reverberatory furnaces by means of atmospheric oxygen. An important improvement was made in the process by Stromeyer by the introduction of a certain quantity of lime together with the potash. Not only was a saving of alkali thus effected, but the oxidation was rendered easier, inasmuch as the whole mass did not fuse, and therefore remained porous and more capable of absorbing the atmospheric oxygen. The chrome-iron ore is first roasted and 4½ parts of the finely ground ore mixed with 2¼ parts of potassium carbonate and 7 parts of lime. This mass after drying at 150° is heated to bright redness with an oxidising

flame, the whole being constantly stirred. At the end of the operation the charge is withdrawn from the furnace and after cooling it is lixiviated with the minimum amount of hot water. If calcium chromate be found in solution a hot saturated solution of potassium sulphate is added, when the lime is thrown down as sulphate and potassium chromate remains in solution. The liquor is next treated with the requisite quantity of sulphuric acid, diluted with twice its volume of water, to convert the chromate into dichromate, and then allowed to cool. The solution of chromate saturated at 16° contains nearly 1 part of salt to 2 parts of water, whilst the dichromate requires 10 parts of water for its solution; hence when the saturated solution of chromate is converted into dichromate, a precipitate of about three-quarters of the dichromate will be formed on cooling. The precipitate is collected and then recrystallised. The mother-liquor, which contains potassium sulphate, is used for the lixiviation of another portion of the roasted mass.

Potassium dichromate crystallises in splendid garnet-red tables or prisms belonging to the asymmetric system, having a specific gravity of 2·692 at 3·9°. It melts below a red-heat, forming a transparent red liquid, which when slowly cooled solidifies in crystals which have the same form as those deposited from aqueous solution. It decomposes at a white heat into oxygen, chromic oxide, and the normal salt. One hundred parts of water dissolve:

At	0°	10°	40°	80°	100°
$K_2Cr_2O_7$	4·96	8·47	29·15	73·00	102·04.

The saturated solution boils at 104°. Potassium dichromate has an acid reaction, a cooling bitter metallic taste, and is insoluble in alcohol; it acts as a powerful poison, probably on account of its oxidising properties. The commercial salt is usually almost chemically pure, and is employed for the preparation of the other chromium compounds, as a reagent, and as an oxidising agent, as well as being largely used in dyeing and calico-printing.

A film of organic matter saturated with a solution of potassium dichromate acquires a dark colour on exposure to light, owing to a reduction to chromic oxide taking place, and a solution of this substance in gelatine is used as a sensitive agent in the Autotype and other similar *photographic printing* processes.

These processes depend not merely upon the de-oxidation of the dichromate, but also upon the fact that this reduction renders the gelatine insoluble in, and non-absorbent of, water, so that those portions of the gelatine-film which have been acted upon by the light remain unchanged when the film is immersed in hot water, while those parts which have been protected from the action of the light dissolve away entirely. A film is thus obtained in which the various shades of the original negative are represented by deposits of varying thickness of the insoluble gelatine, which can be coloured with any desired pigment, and in this way the red- or blue-chalk drawings of the old masters can be produced in exact fac-simile.[1]

Potassium dichromate forms a double salt with mercuric chloride, $K_2Cr_2O_7 + HgCl_2$, which separates out in red well-developed rhombic crystals.

Potassium Trichromate, $K_2Cr_3O_{10}$, is formed by the action of chromic acid solution on the dichromate, but is best prepared by boiling the dichromate with nitric acid of sp. gr. 1·19; on cooling potassium nitrate first separates almost completely, and the decanted liquor then deposits the trichromate in deep-red monosymmetric prisms, having a specific gravity of 2·648. It is decomposed by hot water into chromic acid and the dichromate, and cannot therefore be recrystallised in this manner.[2]

Potassium Tetrachromate, $K_2Cr_4O_{13}$, is obtained by heating the dichromate with nitric acid of specific gravity 1·41, and separates out on cooling in brownish red crusts consisting of small rhombic plates. It has a specific gravity of 2·649, and, like the trichromate, is decomposed by water into chromic acid and the dichromate. The compound described by Darmstädter as potassium nitrochromate is identical with the tetrachromate.[3]

Normal Sodium Chromate, $Na_2CrO_4 + 10H_2O$.—This is obtained by fusing chromic oxide and sodium nitrate together, and evaporating the solution at a low temperature, or by allowing a solution of potassium chromate saturated with soda to evaporate at 0°. The salt is deposited in deliquescent transparent yellow prisms, isomorphous with Glauber's salt. Heated to above 30° the anhydrous salt separates out. It has an alkaline

[1] For a full and interesting description of these processes, see Abney's *Treatise on Photography*. (Longmans.)

[2] Jäger and Krüss, *Ber.* 1889, **22**, 2038.

[3] Wyruboff, *Bull. Soc. Chim.* 1881 (2), **35**, 162.

reaction, and a bitter metallic taste. *Sodium Dichromate*, $Na_2Cr_2O_7 + 2H_2O$, crystallises in thin asymmetric yellowish-red deliquescent prisms. This salt is now manufactured on a large scale, and is much more soluble than the potassium salt.

Ammonium Chromate, $(NH_4)_2CrO_4$—This salt can only be obtained pure from solutions containing excess of ammonia, as it readily loses the latter, forming the dichromate. It is obtained in monosymmetric golden yellow needles, by gently warming pure chromium trioxide with a quantity of ammonia of specific gravity 0·90, which is just sufficient to dissolve the chromate formed, and cooling the solution in a freezing mixture. The *dichromate*, $(NH_4)_2Cr_2O_7$, is readily obtained by adding the requisite quantity of chromium trioxide to ammonia, and separates out on evaporation in orange red monosymmetric crystals, having a specific gravity of 2·367. These are stable in the air, but decompose on ignition into nitrogen, water and a bulky leaf-like mass of chromium sesquioxide. This salt forms a number of crystalline double salts with mercuric chloride.[1] The *trichromate* and *tetrachromate* have also been prepared.

467 Most of the other metals form chromates or basic chromates which are for the most part coloured substances insoluble in water, many of which are largely used as pigments. The most important of these are the following.

Copper Chromates.—Copper dichromate, $CuCr_2O_7 + 2H_2O$, is obtained by the action of concentrated chromic acid solution on copper hydroxide. It forms blackish-brown deliquescent crystals. The solution when boiled deposits the basic salt $Cu_3CrO_6 + 2H_2O$ as a brown precipitate, which is also obtained when boiling solutions of normal potassium chromate and copper sulphate are mixed. Cold solutions, on the other hand, yield the double salt $K_2CrO_4 + Cu_3Cr_2O_9 + 2H_2O$, which is obtained also by the action of potassium dichromate solution on freshly precipitated copper hydroxide in pale brown microscopic six-sided tables. The mineral vauquelinite, $(Cu,Pb)_3Cr_2O_9$, occurs in small glistening monosymmetric crystals or earthy masses, together with crocoisite.

Silver Chromate, Ag_2CrO_4, is obtained as a brick red precipitate when a dilute solution of potassium chromate is poured into a concentrated solution of silver nitrate; the product is however never quite pure, and to obtain it in this condition silver dichromate must be boiled for a long time with water.

[1] Jäger and Krüss, *Ber.* 1889, **22**, 2047.

It then forms a deep green powder, which is insoluble in water, but dissolves with some difficulty in sulphuric acid, nitric acid and ammonia. The solution obtained by dissolving it in as small a quantity as possible of warm ammonia of specific gravity 0·94 deposits ammonio-silver chromate, $Ag_2CrO_4,4NH_3$, on cooling in long yellow needles belonging to the quadratic system.[1]

Silver Dichromate, $Ag_2Cr_2O_7$, is obtained by the action of potassium dichromate on silver nitrate in acid solution; it forms small red asymmetric crystals, which are decomposed by boiling water into chromic acid and the normal chromate.

Barium Chromate, $BaCrO_4$, is an insoluble yellow precipitate, having a specific gravity of 3·9. It is insoluble in acetic, but easily soluble in nitric, hydrochloric, and aqueous chromic acids. From the last solvent the salt $BaCr_2O_7+2H_2O$ may be obtained in yellow stellar needles, which are decomposed by water with separation of the normal salt. Barium chromate is used as a pigment under the name of *yellow ultramarine* or *lemon yellow*.

Zinc Chromates.—Potassium chromate gives with zinc sulphate a yellow precipitate of basic zinc chromate, $Zn_2(OH)_2CrO_4+H_2O$. A similar compound, $2Zn_2(OH)_2CrO_4+H_2O$, is formed when zinc carbonate is heated with a solution of chromic acid.

If zinc oxide or a zinc salt is boiled with potassium dichromate the yellow insoluble compound, $Zn_4(OH)_6CrO_4$, is precipitated.

The chromate obtained by the addition of a hot neutral solution of zinc sulphate to potassium chromate forms a stable yellow pigment sold under the name of *Zinc yellow* or *Buttercup yellow*.

Lead Chromate, $PbCrO_4$, occurs as crocoisite in translucent yellow monosymmetric prisms, having a specific gravity of 5·9 to 6·1. The mineral is found in Siberia, in the Urals, Brazil, Hungary, and the Philippine islands. Crystals having a specific gravity of 6·118 are artificially obtained when lead chloride is strongly heated with potassium chromate, as well as when solutions of lead acetate and normal potassium chromate are allowed slowly to diffuse into one another.[2] A bright yellow precipitate of the normal chromate is obtained when a solution of a lead salt is precipitated with potassium dichromate. This goes under the name of *chrome yellow*, *Paris yellow*, or *Leipsic yellow*, and is largely used as a pigment. It is insoluble in water, but is readily dissolved by nitric acid and caustic potash.

[1] Muthmann, *Ber.* 1889, **22**, 2051.

[2] Drevermann, *Annalen*, 1853, **87**, 121.

When strongly heated it fuses to a brown liquid, which on cooling solidifies to a crystalline mass. As lead chromate at a red-heat oxidises all organic substances, it is frequently employed in organic analysis, especially in the case of bodies which contain chlorine, sulphur, &c. The chrome yellow of commerce often contains admixtures, especially lead sulphate. This, however, is not always to be considered as an adulteration, as it is used for the preparation of a light shade. This is termed *Cologne yellow*, and is obtained by a precipitation of the mixture of the nitrates of lead and calcium with a mixture of sodium sulphate and potassium chromate, or more generally by heating lead sulphate with a solution of potassium dichromate.

Calico is printed or dyed with chrome yellow, by first mordanting the cloth with a solution of lead salt, and afterwards steeping it in one of chromate of potassium.

Basic Lead Chromate, Pb_2CrO_5, occurs in commerce as *chrome red*, and is obtained as a fine red powder by digesting chrome yellow with cold caustic soda, or boiling it with a solution of normal potassium chromate, or by fusing it with nitre. Another basic salt, $Pb_3Cr_2O_9$, occurs as the mineral phœnicite in hyacinth-red crystals, having a specific gravity of 5·75. It may be artificially prepared together with the normal chromate by allowing solutions of lead nitrate and potassium chromate to diffuse into one another, when it separates in dark-red tables.

By making a suitable mixture of chrome yellow and chrome red, or by modifying the process of manufacture so as to obtain a mixture of the two, pigments of any shade between the two may be obtained. These are known commercially as *chrome orange*.

Chromate of Bismuth.—When normal potassium chromate is added to a solution of bismuth nitrate a lemon-yellow finely crystalline precipitate is thrown down, having the composition $Bi_6Cr_2O_{15} = 2(BiO)_2CrO_4 + Bi_2O_3$. This compound does not fuse and is not decomposed on heating. When treated with a quantity of nitric acid insufficient to dissolve it, it is converted into $Bi_2Cr_2O_9 = (BiO)_2Cr_2O_7$; and this salt is also obtained by adding a solution of bismuth nitrate, as nearly as possible neutral, to an excess of a solution of potassium dichromate. It is an orange-yellow crystalline powder which decomposes on ignition and becomes of a dark-green colour. If a few drops of nitric acid be added to the liquid after precipitation and the whole boiled for a few hours, a cinnabar-red crystalline salt,

$(BiO)_2CrO_4$, is thrown down, which on boiling with moderately strong nitric acid partially dissolves and is partially converted into ruby-red crystals having the formula $Bi_2Cr_4O_{15}+H_2O$.[1] Other polychromates of bismuth have been prepared.[2]

Chromic Chromate, $Cr_2O_3.CrO_3=3CrO_2$.—This compound, also known as *chromium dioxide*, is formed when chromic nitrate is gently heated. It is likewise prepared by the partial reduction of the trioxide, and by the precipitation of a chromic salt with a soluble chromate. The brown powder thus obtained is easily soluble in acids. Alkalis precipitate chromic hydroxide from its solution, whilst a chromate remains in the liquid. If chromic chromate be washed for some time with water, it is decomposed into soluble trioxide and insoluble sesquioxide. When nitric oxide is passed into a tolerably concentrated solution of potassium dichromate, chromic chromate is obtained as a dark brown precipitate, which dries at 250° to form a black hygroscopic powder, and this, when heated in a current of hydrochloric acid, yields chromic oxide, water, and chlorine.

When the vapour of chromic chloride is passed through a red-hot tube, violet translucent prisms, having the composition $Cr_5O_9=2Cr_2O_3+CrO_3$, are obtained. These are magnetic, and on ignition are gradually converted into chromic oxide.[3]

Halogen and Amido-Derivatives of Chromic Acid.

468 *Chromyl Fluoride*, CrO_2F_2.—This substance was first obtained by Unverdorben, by the action of sulphuric acid on a mixture of lead chromate and fluorspar, and was regarded by him as chromium hexafluoride. Olivieri has, however, shown that it only contains two atoms of fluorine to one of chromium, and is in reality derived from chromic acid by the replacement of the two hydroxyl groups by fluorine. It is best prepared by heating 60 grams of well-dried potassium dichromate and 30 grams of fluorspar with 100 grams of fuming sulphuric acid in a platinum retort. It condenses in a freezing mixture to a blood-red very volatile liquid, which is converted even by the moisture of the air into chromic fluoride and chromic acid.

Potassium Fluochromate, $F.CrO_2.OK$, is formed by heating potassium dichromate with hydrofluoric acid in a platinum

[1] Muir, *Journ. Chem. Soc.* 1876, ii. 12.
[2] *Journ. Chem. Soc.* 1877, i. 24, 645.
[3] Geuther, *Annalen*, 1861, **118**, 61.

vessel, and crystallises in red quadratic pyramids, which are soluble in water. The solution decomposes on boiling into potassium dichromate and hydrofluoric acid.

Chromyl Chloride, CrO_2Cl_2, appears to have been discovered by Thomson,[1] and was then investigated by Berzelius and Wöhler.[2] It is prepared by distilling a fused mixture of ten parts of common salt and twelve parts of potassium dichromate, together with thirty parts of concentrated sulphuric acid, and, in order to remove free chlorine repeatedly rectifying the distillate in a current of carbon dioxide. It is also formed by heating chromium trioxide in a current of hydrochloric acid, when it distils over, and an oily liquid remains which probably is *chlorochromic acid*, $Cl.CrO_2.OH$. Chromyl chloride is a mobile liquid of a splendid blood-red colour by transmitted, and nearly black by reflected light. It boils at 115·9°, and has a specific gravity at 25° of 1·920.[3] It absorbs chlorine readily, dissolves iodine, and when dropped into water it remains unaltered for a few seconds, but is afterwards decomposed with violent ebullition into chromic and hydrochloric acids. The specific gravity of the vapour of chromyl chloride is, according to Bineau, 5·39, corresponding to the above formula. When brought into contact with phosphorus it explodes, whilst it takes fire in contact with sulphur, hydrogen sulphide, ammonia, alcohol, and many other organic bodies, and when diluted with acetic acid, acts as an oxidising and chlorinating agent upon hydrocarbons. When heated in a closed tube to 180° for three or four hours *trichromyl chloride*, $Cr_3O_6Cl_2$, is formed as a black powder, which deliquesces on exposure to the air.[4]

Bromine and iodine do not form analogous chromyl derivatives, but when a bromide or iodide is heated with sulphuric acid and potassium dichromate free bromine or iodine is obtained. This reaction is made use of for the qualitative detection of chlorine in presence of bromine or iodine, as if chlorine is present the substance yields chromyl chloride when heated with potassium dichromate and sulphuric acid, and the latter by the action of water is converted into chromic acid, which may be recognised by the usual tests.

Potsasium Chlorochromate, $Cl.CrO_2.OK$, was discovered by Péligot,[5] and is formed when three parts of potassium dichro-

[1] *Phil. Trans.* 1827, p. 159. [2] *Pogg. Ann.* 1834, **33**, 343.
[3] Thorpe, *Journ. Chem. Soc.* 1880, i. 327.
[4] *Journ. Chem. Soc.* 1870, 31. [5] *Journ. Pharm.* June, 1833.

mate are gently heated with four parts of concentrated hydrochloric acid and a small quantity of water, or by adding chromyl chloride to a saturated solution of potassium chloride:

$$CrO_2Cl_2 + KCl + H_2O = KCrO_3Cl + 2HCl.$$

It crystallises in flat red rectangular prisms, having a specific gravity of 2·497. The salt is partially decomposed by water, but may be recrystallised from water containing hydrochloric acid. It decomposes at 100°, with evolution of chlorine:

$$4CrO_2(OK)Cl = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_2.$$

Other chlorochromates have been described by Péligot and by Prætorius.[1]

Potassium Amidochromate, $NH_2.CrO_2.OK$, is formed by passing ammonia into ether containing the chlorochromate in suspension. The product is dissolved after 24 hours in water, filtered from an insoluble substance simultaneously formed, and the solution evaporated. The amidochromate crystallises out in garnet-red monosymmetric prisms, which are only slowly decomposed by boiling water, and somewhat more rapidly by caustic potash. On treatment with nitrous acid it yields nitrogen and potassium dichromate.

$$2CrO_2(OK)NH_2 + 2HNO_2 = 2N_2 + 3H_2O + K_2Cr_2O_7.$$

Perchromic Acid, $HCrO_4$.—A deep indigo-blue coloured solution is obtained when hydrogen dioxide is added to an aqueous solution of chromium trioxide, or to a solution of a chromate acidified with sulphuric acid. If the freshly-prepared solution be shaken with ether, this liquid takes up the perchromic acid and becomes of a dark-blue colour. The ethereal is more stable than the aqueous solution, but on evaporation it leaves a residue of chromium trioxide. The same decomposition is effected by alkalis, a chromate being formed with evolution of oxygen. The colouring power of perchromic acid is so great that its formation is employed as a most delicate test, both for chromic acid and for hydrogen dioxide. The deepest coloration is produced when two molecules of hydrogen dioxide are used to one molecule of chromium trioxide.

The constitution of the substance thus formed is as yet uncertain. It has been variously regarded as $Cr_2O_7 + xH_2O$,[2]

[1] *Annalen*, 1880, **201**, 1.

[2] Barreswil, *Ann. Chim. Phys.* 1847 (3), **20**, 364.

$CrO_6 + 3H_2O$,[1] $CrO_3 + H_2O_2$,[2] and $2HCrO_4 + H_2O_2$.[3] By the action of sodium dioxide on a thin paste of chromic hydroxide and water Häussermann[4] obtained a sodium salt having the composition $Na_6Cr_2O_{15} + 28H_2O$, which would be the salt of an acid derived from the anhydride CrO_6. When this salt is treated with sulphuric acid, the above characteristic blue colour is first produced, but oxygen is soon evolved, and chromic sulphate remains in solution.

Chromous Salts.

469 *Chromous Chloride*, $CrCl_2$, is formed by the ignition of chromium in hydrogen chloride or of chromic chloride in a current of hydrogen gas free from oxygen, and forms white, silky, lustrous needles which are stable in dry air. It dissolves in water, with evolution of heat, forming a blue solution, which absorbs oxygen with extreme avidity yielding basic chromic salts, and forms a powerful reducing agent. This solution is best obtained as follows: 300—400 grams of granulated zinc and 50 grams of very finely powdered potassium dichromate are placed in a flask of about 3 litres capacity, and a mixture of 300 c.c. of pure fuming hydrochloric acid and 200 c.c. of water added. On agitation a violent reaction occurs, the liquid becoming first green from the intermediate formation of chromic salts, but after a few minutes a clear sky-blue solution remains, which may be directly employed as a reducing agent. To obtain pure chromous chloride from the solution, sodium acetate is added to the liquid, the precipitated chromous acetate washed with water saturated with carbon dioxide, redissolved in hydrochloric acid, and a current of hydrochloric acid gas passed into the cooled solution. All these operations must be performed in an atmosphere free from oxygen. The chromous chloride is thus obtained in blue needles containing 4 molecules of water.[5]

The vapour density of chromous chloride at 1300° was found by Nilson and Pettersson to be 7·8, considerably lower than is required by the formula Cr_2Cl_4. At 1600° the density is further

[1] Fairley, *Chem. News*, 1876, **33**, 337.
[2] Moissan, *Compt. Rend.* 1883, **97**, 96.
[3] Berthelot, *Compt. Rend.* 1889, **108**, 25.
[4] *J. Pr. Chem.* 1893 (2), **48**, 70.
[5] Recoura, *Ann. Chim. Phys.* 1887 (6), **10**, 9.

reduced to 6·2, showing that probably at a higher temperature its density would finally reach 4·25, corresponding to $CrCl_2$.[1]

Chromous Bromide, $CrBr_2$, is obtained by gently heating chromic bromide in hydrogen gas; also by heating the metal in gaseous hydrobromic acid. It is a white crystalline mass yielding a green basic chromic bromide on exposure to the air.

Chromous Iodide, CrI_2, is a crystalline mass obtained by heating chromium in gaseous hydriodic acid.[2]

Chromous Sulphide, CrS, is obtained by igniting chromous chloride in sulphuretted hydrogen, or by the long continued heating of chromic sulphide in hydrogen, and forms a black powder which is only attacked with difficulty by acids.[3] It may be also prepared by heating chromium to a very high temperature in sulphuretted hydrogen, when it is obtained in prismatic needles having a specific gravity of 4·08, and sufficiently hard to scratch quartz.[4]

Chromous Sulphate, $CrSO_4 + 7H_2O$, is prepared by dissolving the metal in dilute sulphuric acid. It is best obtained by dissolving chromous acetate in dilute sulphuric acid; on cooling it separates out in fine blue crystals isomorphous with ferrous sulphate. The ammoniacal solution absorbs oxygen, nitric oxide, and acetylene. If potassium sulphate be dissolved in a cold saturated solution of the chloride, and then alcohol added until a precipitate begins to form, the mass being allowed to stand for some weeks in absence of air, fine blue rhombic prisms, having the composition $K_2SO_4 + CrSO_4 + 6H_2O$, are deposited, and these soon become green on exposure to the air from absorption of oxygen.

Chromous Carbonate, $CrCO_3$, is obtained by precipitating the chloride with potassium carbonate. A yellow to greenish-blue precipitate is obtained in the cold, and this assumes a reddish-brown colour on warming.

Chromous Acetate is a red crystalline precipitate obtained by pouring a solution of chromous chloride into a saturated solution of sodium acetate.

[1] *Journ. Chem. Soc.* 1888, i. 830.
[2] Moissan, *Compt. Rend.* 1891, **92**, 1051.
[3] Moissan, *Compt. Rend.* 1880, **90**, 817.
[4] Moulot, *Compt. Rend.* 1895, **121**, 943.

Chromic Salts.

470 The normal chromic salts have a blue or violet colour, and allow red light to pass through their solutions. The cold solutions have a violet colour, which on heating changes to green; in some cases the solution immediately becomes violet on cooling, but in others this only occurs on allowing the cooled solution to stand for some time. Only the violet solutions of the salts with oxy-acids yield crystalline salts, the green solutions depositing an amorphous mass on evaporation. Many attempts have been made to explain the changes which take place, and much light has of late been thrown on the subject by the researches of Recoura and others. The salts which have been most closely examined are the chloride, bromide, and sulphate.

In the case of the chloride and bromide it appears that each exists in a violet and a green modification, both of which can be obtained crystalline, and combined with the same number of molecules of water; the former modification exists in dilute solution and the latter in concentrated solutions, or in solutions containing an excess of acid. In addition a different chloride is obtained by dissolving the hydroxide, $Cr_2O(OH)_4$, in hydrochloric acid, and has probably the composition, Cr_2OCl_4. In the case of the sulphate and probably of the other oxy-acid salts, the green solution contains complex derivatives of the same hydroxide, $Cr_2O(OH)_4$ (p. 845).

Chromium and the Halogens.

Chromic Fluoride, CrF_3.—The anhydrous salt is obtained by passing hydrogen fluoride over heated chromic chloride, and sublimes at a high temperature in slender needles. The crystallised fluoride, $CrF_3 + 9H_2O$, is obtained by adding ammonium fluoride to a cold solution of chromic sulphate. It is sparingly soluble in water, but dissolves in hydrochloric acid, forming a violet solution. When heated in the air it becomes green, and finally leaves a residue of chromium trioxide.[1]

Chromic Chloride, $CrCl_3$.—The anhydrous chloride is obtained by heating an intimate mixture of chromic oxide and carbon in a stream of dry chlorine. It forms peach-blossom coloured scales, which have a specific gravity of 3·03. These volatilise at 1,065°, yielding a vapour of the density 6·135, the formula

[1] Poulenc, *Compt. Rend.* 1891, **116**, 253; Fabris, *Gazzetta*, 1890, **20**, 582.

$CrCl_3$ requiring 5·478, and Cr_2Cl_6 corresponding to a density twice as great; hence this latter compound cannot exist in the state of vapour. From 1190° up to 1300° the density is 5·5 (Nilson and Pettersson). Chromic chloride is almost insoluble in cold water, but it is readily soluble in presence of a very small quantity (less than 0·001 per cent.) of chromous chloride, cuprous chloride, or stannous chloride. The dilute solutions of the chloride have a violet colour, whilst the concentrated solutions or those containing a large excess of acid are green. Recoura[1] has shown that the heat evolved by the action of an equivalent quantity of soda is nearly 50 per cent. greater in the case of the green solutions, and that as the concentration of the solution increases, the evolution of heat gradually increases from the value for the violet solution (+ 22·2 cal.) to that of the green (+ 31·5 cal.). The colour of the solution at the same time gradually changes from violet to pure green, thus indicating a gradual transition of the violet into the green modification. Recoura has succeeded in isolating both modifications in the crystalline form: the green chloride separates out in small emerald green crystals when a current of hydrogen chloride is passed through a well-cooled, saturated solution of chromic chloride; these have the composition $2CrCl_3 + 13H_2O$, or according to Marchetti,[2] $CrCl_3 + 6H_2O$. If the crude chloride be dissolved in its own weight of water, warmed for a few minutes to 80°, and then cooled to 0°, the solution contains both green and violet salt, and on passing hydrogen chloride only the latter separates out at first and may be obtained free from the green modification if it is immediately filtered off. It forms grey crystals containing the same number of molecules of water as the green salt, and dissolves in water forming the characteristic blue-violet solution. Both of the salts immediately react with three equivalents of soda yielding one and the same chromic hydroxide.

The exact nature of these two isomerides is not known, but it is probable from the result of cryoscopic experiments that the green salt is of a more complex nature, having a higher molecular weight (Marchetti).

Another chloride may be obtained in solution by the action of hydrochloric acid on the hydroxide $Cr_2O(OH)_4$. This has a less bright colour than the green salt described above, and only

[1] Recoura, *Ann. Chim. Phys.* 1887 (6), **10**, 5.
[2] Marchetti, *Gazzetta*, 1892, **22**, 375.

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reacts with two equivalents of soda, and has therefore probably the composition Cr_2OCl_4, and corresponds to the green salts formed by heating the solutions of the salts of chromium with oxy-acids. In presence of hydrochloric acid it is slowly converted into one or other of the above trichlorides according to the concentration of the solution.

Chromic Bromide, $CrBr_3$.—The anhydrous compound is prepared in a similar way to the chloride. It forms black semi-metallic translucent hexagonal scales, having an olive-green colour, and exhibits in one direction a fine red dichroism. In its properties it closely resembles the chloride, and dissolves easily in water, when a small quantity of chromous bromide, or any other reducing agent, such as tinfoil, is present. Solutions of chromic bromide behave in an analogous manner to those of the chloride, and yield two isomeric salts, the one forming blue-grey, and the other green crystals, both of which have the composition $CrBr_3 + 6H_2O$.[1]

Chromic Iodide, CrI_3 is unknown.

Chromium and Sulphur.

471 *Chromium Sesquisulphide*, or *Chromic Sulphide*, Cr_2S_3.—This is obtained by heating chromium with sulphur, or by igniting chromic chloride, or the trioxide, in a current of hydrogen sulphide. It forms either a blackish-grey metallic lustrous powder, or an elastic mass having a specific gravity of 3·77. When heated in the air it burns with formation of the green oxide, and in chlorine yields chloride of sulphur and chromic chloride. It is not attacked by nitric acid. This compound cannot be prepared in the wet way, as soluble sulphides precipitate the hydroxide from chromic salts, with liberation of sulphuretted hydrogen:

$$2CrCl_3 + 6H_2O + 3(NH_4)_2S = 2Cr(OH)_3 + 6NH_4Cl + 3H_2S.$$

Chromic Sulphate, $Cr_2(SO_4)_3$, is obtained by mixing equal parts of concentrated sulphuric acid and chromium hydroxide dried at 100°. The mixture is allowed to stand in a loosely-stoppered bottle, when the solution, which, to begin with, is green, becomes blue, and in some weeks deposits a violet-blue crystalline mass, which is purified by solution in water and precipitation with alcohol. Thus obtained, it is a violet

[1] Recoura, *Compt. Rend.* 1890, **110**, 1029.

crystalline powder; if a smaller quantity of alcohol be added blue octohedra containing 18 molecules of water are deposited. Chromic sulphate and the sulphates of the alkali metals form double salts, corresponding to the alums, to which the name of *chrome-alums* is given.

Potassium Chromic Sulphate or *Chrome-Alum*, $K_2SO_4 + Cr_2(SO_4)_3 + 24H_2O$.—This substance is best obtained by the reduction of a solution of potassium dichromate, $K_2Cr_2O_7$, by adding the requisite quantity of sulphuric acid, and passing sulphur dioxide through the solution:

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

In place of sulphur dioxide any other easily oxidisable substance, such as alcohol, &c., may be employed, but in this case more sulphuric acid must be added. Chrome-alum is now obtained in large quantity as a by-product in the manufacture of artificial alizarine from anthracene, $C_{14}H_{10}$, in which the hydrocarbon is treated with a mixture of sulphuric acid and potassium dichromate, when oxy-anthracene (anthraquinone) $C_{14}H_8O_2$, is formed, and this is then subjected to further treatment. The salt crystallises in large dark purple-red, almost black, octohedra, which, when seen by transmitted light, exhibit a ruby-red colour. It dissolves in seven parts of water at the ordinary temperature. The solution has a dingy blue colour, with a tinge of red, which, when heated to 70°, becomes dark-green. After standing for several months, however, it returns to its ordinary colour (see below). Chrome-alum is used in dyeing and calico-printing, as well as in tanning.

Ammonium Chromic Sulphate, $(NH_4)_2SO_4 + Cr_2(SO_4)_3 + 24H_2O$ is obtained by crystallising a mixture of the two salts, or by reducing ammonium dichromate. The salt is less soluble than the potassium compound, and easily crystallises in fine ruby-red octohedra, which have a specific gravity of 1·738.

A number of other crystalline double chromic sulphates, both anhydrous and containing water of crystallisation, have been described.[1]

Action of Heat on Chromic Sulphate and its Double Salts.—When the cold violet solution of chromic sulphate is boiled or the crystals heated to 100°, a green salt is obtained, which, unlike the violet salt, is soluble in alcohol, and does not crystallise on evaporation. This change has been examined by many

[1] Klobb, *Compt. Rend.* 1893, **117**, 311; *Bull. Soc. Chim.* 1893 (3), **9**, 663.

chemists, some of whom have attributed it to the formation of an isomeric modification, and others to the formation of a basic salt. As with the halogen derivatives, more complete investigations, especially those of Recoura, have thrown much light on the nature of the phenomenon. Recoura [1] has shown that in the boiled solution, one-sixth of the sulphuric acid is in the free state, and that therefore the green salt formed has the empirical formula $2Cr_2O_3,5SO_3$. When the recently boiled solution is treated with barium chloride in the cold, only one-third of the total sulphuric acid is precipitated as barium sulphate. As the whole of the free sulphuric acid would be thus precipitated, only one of the SO_3 groups in the above compound is precipitable as barium sulphate in the cold, and the remaining SO_3 groups must be combined with the chromium to form a complex basic radical of which the green salt is the sulphate. The change may be formulated as follows :—

$$2Cr_2(SO_4)_3 + H_2O = [Cr_4O(SO_4)_4]''SO_4 + H_2SO_4.$$

In confirmation of this is the fact that the green salt, when treated with an excess of caustic soda, yields the hydroxide $Cr_2O(OH)_4$. The green salt may therefore be regarded as the sulphate of the hypothetical compound *sulphochromyl hydroxide*, $[Cr_4O(SO_4)_4](OH)_2$.

The above green salt is an unstable substance, and when the solution is allowed to stand in the cold it is gradually reconverted into the violet sulphate, from which the whole of the sulphuric acid may be precipitated by barium chloride in the cold, and which yields with caustic potash the trihydroxide, $Cr(OH)_3$.

The double salts, such as chrome alum, undergo an analogous reaction when their solutions are heated, and the solutions regain their violet colour on standing in the cold. It is probable that similar complex salts are formed in the case of the other chromic salts, as their solutions become green on boiling ; but in these cases the compound formed is much less stable, and is immediately reconverted into the normal salt on cooling.

Green Modification of Chromic Sulphate.—In addition to the above complex basic sulphate, a green salt of the same empirical

[1] Recoura, *Ann. Chim. Phys.* 1895 (7), **4**, 494 ; Favre and Valson, *Compt. Rend.* 1872, **74**, 1023 ; Whitney, *Zeit. phys. Chem.* 1896, **20**, 40 ; Dougal, *Journ. Chem. Soc.* 1896, i. 1526.

formula as the normal violet salt is known, which, however, possesses entirely different properties.[1] This is obtained by heating the crystals of the violet salt, $Cr_2(SO_4)_3+18H_2O$, at 90° until they have the composition $Cr_2(SO_4)_3+8H_2O$. The resulting green compound is readily soluble in water, but the freshly prepared solution shows neither the ordinary reactions of a chromium salt nor of a sulphate. In the course of a few days the solution is gradually transformed into the normal violet sulphate.

This green compound combines with one, two, or three molecules of sulphuric acid, or with the equivalent quantities of a sulphate yielding substances from which no barium sulphate can be obtained by precipitation in the cold; these may be regarded as the complex acids, chromosulphuric acid, $[Cr_2(SO_4)_4]H_2$, chromodisulphuric acid, $[Cr_2(SO_4)_5]H_4$, and chromotrisulphuric acid, $[Cr_2(SO_4)_6]H_6$, or their salts. These are quite stable in the dry state and in dry air, but in solution gradually undergo conversion into the normal chromium salts. The alkali chromosulphates are isomeric with the chrome alums, from which they may be readily obtained by heating the crystals of the latter for some time at 90°. *Potassium chromosulphate*, $[Cr_2(SO_4)_4]K_2+4H_2O$, is thus obtained as a green salt which dissolves slowly but completely in cold water.

The constitution of the green sulphate is at present unknown, but Recoura regards it as corresponding to the crystallised green chloride described above.

Sulphochromic Hydroxide, $[(SO_3)_4Cr_2O_2](OH)_2$.—When the green sulphate is treated with four, five, or six molecules of sulphuric acid and the product heated for some time to 115°, transparent vitreous products are obtained, having a bottle-green colour, much less distinct than that of the other green chromium derivatives. These dissolve in water, forming opaline solutions having a slight yellowish-green colour, which yield precipitates with all solutions of metallic salts, including those of the alkali metals. The solution of the product obtained by heating the green sulphate with four molecules of sulphuric acid gives, for example, a precipitate with potassium chloride having the composition $[(SO_3)_4Cr_2O_2](OK)_2$, and with copper chloride one of the composition $[(SO_3)_4Cr_2O_2]O_2Cu$. In all these salts the metal is in combination with the chromium and not with the sulphuric acid, as on treatment with an excess of alkali they yield

[1] Recoura, *Ann. Chim. Phys.* 1895 (7), **4**, 505.

the chromites, the reaction with the copper salt being as follows:—

$$[(SO_3)_4Cr_2O_2]O_2Cu + 8NaOH = 4Na_2SO_4 + Cr_2O_3,CuO + 4H_2O.$$

They are therefore termed the *sulphochromites.*[1]

Chromium Nitrogen and Phosphorus.

472 *Chromium Nitride,* NCr, is formed by the direct union of its elements at a red-heat[2]; and also by passing ammonia over heated chromic chloride. It is a brownish-black powder, which takes fire and burns when heated to 200° in the air or in oxygen. Cold chlorine does not act upon it, but when heated in this gas small explosions first occur, owing to formation of nitrogen chloride, and at last chromic chloride remains. It does not undergo change on ignition in hydrogen or in aqueous vapour, and is not attacked by caustic potash, hydrochloric acid, or nitric acid. Concentrated sulphuric acid converts it into ammonium chrome-alum:

$$2CrN + 4H_2SO_4 = Cr_2(SO_4)_3 + (NH_4)_2SO_4.$$

Chromic Nitrate, $Cr(NO_3)_3 + 9H_2O$, is obtained by dissolving the hydroxide in nitric acid, and crystallises in oblique purple-red prisms. The solution, like that of the sulphate, turns green on boiling and on evaporation dries to a green amorphous mass. The green solution at once becomes violet on cooling.

Chromium Phosphide, PCr, is obtained by passing the vapour of phosphorus over ignited potassium chromate. On lixiviating the black fused mass with water, a crystalline powder remains behind, having a metallic lustre, and possessing the above composition. When heated in oxygen this powder takes fire, and burns with formation of chromic phosphate.

Chromic Phosphates. The violet *phosphate* $CrPO_4 + 6H_2O$ is obtained as a voluminous precipitate by adding a solution of sodium hydrogen phosphate to an excess of chrome alum. When dried at 100° it loses water and becomes green. A green phosphate probably identical with this product is obtained by the addition of an excess of the phosphate to chromic chloride solution, the composition of which is $CrPO_4 + 3H_2O$ according

[1] Recoura, *Ann. Chim. Phys.* 1895 (7), **4**, 516.

[2] Brieglieb and Geuther, *Annalen*, 1862, **123**, 239.

to Rammelsberg, or $2CrPO_4 + 5H_2O$ according to Bloxam. If chromic hydroxide be dissolved in excess of phosphoric acid and the solution evaporated and heated to 316°, *chromic metaphosphate* $Cr(PO_3)_3$ is obtained, which has been employed as a green pigment.

Chromium and Carbon.

473 *Chromium Carbides.* When chromium is heated with an excess of carbon in the electric furnace the carbide C_2Cr_3 is formed, which crystallises in brilliant plates having a fatty lustre, a specific gravity of 5·62 and a hardness intermediate between that of topaz and corundum. The crystals are not attacked by concentrated or dilute acids with the exception of dilute hydrochloric acid, which dissolves them slowly. Water has no action on it at 100°. A second carbide CCr_4 is sometimes found on the ingots of metallic chromium prepared in the electric furnace, in needles 10–20 mm. long. These have a specific gravity of 6·75 and a hardness rather greater than that of quartz.[1]

Cyanogen Compounds of Chromium. Potassium Chromocyanide, $K_4[Cr(CN)_6]^{iv} + 2H_2O$, is obtained by the action of potassium cyanide on chromous acetate and forms blue crystals. It is soluble in water, and on exposure to air passes into the next compound.

Potassium Chromicyanide, $K_3[Cr(CN)_6]^{iii}$, forms light yellow monosymmetric crystals, obtained by pouring a solution of chromic acetate into a boiling solution of potassium cyanide.

Chromic Thiocyanate, $Cr(SCN)_3$. Chromic hydroxide dissolves in thiocyanic acid, yielding a greenish-violet solution which when concentrated over sulphuric acid dries to a dark-green amorphous deliquescent mass. It forms a series of characteristic double salts.[2]

Potassium Chromic Thiocyanate, $Cr(SCN)_3,3KSCN + 4H_2O$, is formed by heating a moderately concentrated solution of 6 parts of potassium thiocyanate and 5 parts of chrome alum for 2 hours to the boiling point: the sulphates formed are precipitated by addition of alcohol, the filtrate evaporated and the residue recrystallised from alcohol. It forms quadratic, almost black crystals, which appear ruby red in transmitted light, and dissolve very readily in water and alcohol, forming a

[1] Moissan, *Compt. Rend.* 1894, **119**, 185.
[2] Rössler, *Annalen*, 1867, **141**, 185.

wine red solution. It is decomposed by alkalis and warm hydrochloric acid. The solution gives precipitates of analogous salts with lead and silver salts.[1]

Ammoniacal Chromium Bases.

474 Like the salts of copper and zinc (p. 340, 502) those of chromium readily combine with ammonia, forming complex salts in which the ammonia is chemically combined with the chromium atoms. As with the copper salts many of these also contain the elements of water in combination with the metal, and the ammonia molecules may also be replaced by other radicals such as the group NO_2. The constitution of these compounds has not yet been satisfactorily explained, and the various theories proposed will be considered under the metals of Group 8, most of which form a large number of analogous derivatives.

The following series of chromammino-compounds have been described:

Tetrathiocyanato-diammine chromites or diamminochromium thiocyanates $[(SCN)_4(NH_3)_2Cr]'M'$.

Chloraquotetrammine chromic or chlorotetrammino-chromium salts $[Cl.H_2O(NH_3)_4Cr]''R'_2$.

Aquopentammine chromic or roseochromium salts $[H_2O.(NH_3)_5Cr]'''R'_3$.

Chloropentammine chromic or purpureochromium salts $[Cl(NH_3)_5Cr]''R'_2$.

Nitritopentammine chromic or xanthochromium salts $[NO_2(NH_3)_5Cr]''R'_2$.

Rhodochromium salts $HO[Cr_2(NH_3)_{10}]H_2OR'_5$.

Rhodosochromium salts $(HO)_3[Cr_2(NH_3)_6](H_2O)_2R'_3$.

where M′ represents a monovalent basic radical, and R′ a monovalent acid radical.

Diammino-chromium thiocyanates. — When finely divided potassium dichromate is added to fused ammonium thiocyanate ammonia is evolved, and the whole mass solidifies. When this is treated with water, filtered, and a few lumps of ammonium chloride added, scales of the salt $[(SCN)_4(NH_3)_2Cr]NH_4$ separate out.

[1] Rossler, *Annalen*, 1867, **141**, 185.

This salt crystallises from solution on slow evaporation in dark red rhombic dodecahedra, which have the exact appearance of small garnets. When warmed with caustic potash these yield the corresponding *potassium* salt $[(SCN)_4(NH_3)_2Cr]K$, which crystallises from water in lustrous red scales. The free acid $[(SCN)_4(NH_3)_2Cr]H$ is obtained by the action of sulphuretted hydrogen on the mercury salt and crystallises with one molecule of water in lustrous red plates.[1]

The remaining series of salts closely resemble the corresponding cobaltammine salts, and are obtained in a similar manner.[2]

Detection and Estimation of Chromium.

475 Chromium oxide is frequently detected in its insoluble compounds by its characteristic green colour, as well as by the fact that it forms an emerald-green bead, both in the oxidising and reducing flame, with borax or microcosmic salt. On fusion with soda and saltpetre a yellow mass is obtained, which is soluble in water, and the solution acidified by acetic acid yields a yellow precipitate with soluble lead salts. Caustic potash or soda gives a green precipitate in solutions of chromic salts. This dissolves in an excess of alkali in the cold, but is completely precipitated on boiling the solution. This reaction is sometimes employed for the separation of chromium from aluminium, metals which are obtained together in the course of analysis. If, however, the solution contains large quantities of a zinc or magnesium salt, alkalis produce insoluble chromites of these metals, and these are precipitated in the following operations, together with iron. In this case the precipitate may be boiled with sodium hypochlorite, or fused with saltpetre and sodium carbonate, the fused mass dissolved in water, and the clear solution tested for a chromate. The detection of chromic acid is rendered easy by the bright yellow or red colour of its salts. The yellow colour of the normal chromates becomes red on the addition of an acid, and again yellow when made alkaline. Silver nitrate precipitates the normal chromates

[1] *Annalen*, 1863, **126**, 113; *Journ. Chem. Soc.* 1861, 252; *J. pr. Chem.* (2), 1892, **45**, 219. See also Nordenskiöld, *Zeit. anorg. Chem.* 1892, **1**, 135.

[2] See Jörgensen, *J. pr. Chem.* (2), 1882, **25**, 414; 1884, **29**, 409; **30**, 1; 1890, **42**, 206; 1892, **45**, 260, 274; *Zeit. anorg. Chem.* 1893, **5**, 147; 1894, **7**, 289; Petersen, *Zeit. physikal. Chem.* 1892, **10**, 580.

of a purple-red, and the dichromates of a dark-red colour, both precipitates being easily soluble in ammonia and in dilute nitric acid. Barium chloride gives a pale yellow precipitate, with solutions of the normal chromates, and lead acetate throws down a pale yellow powder, insoluble in nitric acid, turned red by a slight excess of caustic potash, and soluble in a large excess of this reagent, and from this solution acetic acid again precipitates chrome-yellow. All the chromates are converted by reducing agents into the chromic salts. When they are distilled in the dry state with common salt and sulphuric acid, they yield red vapours of chromyl chloride, which condense to a dark-red liquid, becoming yellow on saturation with ammonia.

The chromium salts do not impart any colour to the non-luminous gas-flame. The spark-spectrum of the metal is a complicated one. The following are the brightest lines:

In the green . . .	5208·8 5207·4 5204·7	In the dark blue .	4289·9 4275·0 4254·5

In order to determine chromium *quantitatively* in the chromium salts, a hot solution is precipitated with a small excess of ammonia, the solution boiled till the free ammonia is nearly all expelled, and the precipitate well washed with hot water, dried, ignited, and weighed as chromic oxide. In the chromates the chromium is either determined by precipitating in acetic acid solution with lead acetate, and weighing the precipitated lead chromate ignited at a dull red-heat, or the solution is mixed with hydrochloric acid and alcohol, or treated with sulphur dioxide, in order to form chromic chloride, which is then determined as above. Another good method is to precipitate the neutral solution, or one made slightly acid by nitric acid, with mercurous nitrate, and to convert the washed and dried precipitate by ignition into chromic oxide.

The amount of chromate may also be estimated volumetrically by determining the amount of a solution of a ferrous salt which a known quantity can convert into a ferric salt, the converse of this process, viz., the titration of a solution of a ferrous salt with standard potassium dichromate being employed for the volumetric estimation of iron. A standard chromate solution is also largely employed in other volumetric processes in which the reaction is one of oxidation.

For the valuation of chrome iron ore a large number of

different methods have been proposed. The mineral is first fused with an alkali and oxidising agent such as borax or sodium carbonate and nitre, or with sodium peroxide, in order to convert the chromium into a soluble chromate, which may be then estimated by the methods already mentioned. For details the works on analytical chemistry must be consulted.

476 *Atomic weight of Chromium.*—The older atomic weight determinations gave numbers varying from 55·6 to 51·4, owing probably to the inexact methods and impure material employed. Berlin[1] in 1845–6 obtained the number 52·15 by the analysis of silver chromate, whilst Kessler[2] in 1861 obtained the number 52·02 from the determination of the equivalent quantities of potassium dichromate and potassium chlorate required to oxidise a given quantity of arsenious oxide to pentoxide. Siewert[3] in the same year found the number 51·72 by the analysis of violet chromic chloride and of silver dichromate, and Baubigny[4] in 1884, the number 51·95 by the conversion of chromic sulphate into the trioxide. In 1889 Rawson,[5] by the conversion of pure ammonium dichromate into chromium trioxide, obtained the atomic weight 51·80, and finally Meinecke[6] in 1891 obtained the average value 51·68 by estimating (1) the quantity of silver and chromium in silver chromate and ammonio-silver chromate; (2) the quantity of oxygen in these two compounds; (3) the quantity of oxygen in potassium dichromate; and (4) the quantity of oxygen and of chromium in ammonium dichromate.

MOLYBDENUM, Mo = 95·3.

477 The name *Molybdæna*, which occurs in the writings of Dioscorides and Pliny, is derived from the Greek word μόλυβδος, lead, and was originally employed for the designation of a variety of substances containing lead. At a later time the name was used to signify galena or substances similar in appearance to this body, and to these the name of

[1] *Annalen*, 1844, **56**, 207; 1845, **60**, 182.
[2] *Pogg. Ann.* 1861, **113**, 137.
[3] *Zeitschr. Ges. Naturwiss.* 1861, **17**, 530.
[4] *Compt. Rend.* 1884, **98**, 146.
[5] *Journ. Chem. Soc.* 1889, i. 213.
[6] *Annalen*, 1891, **261**, 339.

plumbago or black-lead was also given. Even sulphide of antimony and pyrolusite, to which latter mineral Linnæus gave the name of molybdænum magnesii, were also classed among the same group of bodies. At a still later period this word was solely applied to graphite and to the mineral sulphide of molybdenum, which is extremely similar in its appearance to graphite.

The difference between plumbago and the sulphide of molybdenum was first pointed out by Scheele in his treatise on "Molybdæna" in 1778, and in another on "Plumbago" in 1779.[1] By heating the former mineral with nitric acid he obtained sulphuric acid, together with a peculiar white earth which he recognised as an acid-forming oxide, and termed *acidum molybdænæ*, and he assumed that the mineral was a compound of this acid with sulphur. In 1781 Bergman suggested that the earth was probably a calx of a metal, and in 1782 he wrote that Hjelm had succeeded in preparing the metal, though the details of the experiments were first made known in 1790.

Another mineral containing molybdenum is the yellow molybdate of lead or wulfenite first found in Carinthia. This was investigated by the elder Jacquin, and he showed that it contained lead, but was doubtful as to the nature of the acid with which this metal was combined. Salzwedel, who analysed it in 1790, believed that it was a lead salt of tungstic acid, but Klaproth in 1797 ascertained its true composition. The compounds of molybdenum were then more accurately examined by Berzelius.

Molybdenum is usually found as molybdenite, MoS_2; also as wulfenite, $PbMoO_4$; more rarely it occurs as molybdic ochre, $MoO_3 + xH_2O$, and pateraite, $CoMoO_4$. Iron ores frequently contain traces of molybdenum, and hence this metal is also found in pig-iron as well as in the slag. Thus the iron-slag obtained in the process of melting the cuprous schist at Mansfeld, is said to contain from 9 to 28 per cent. of molybdenum.[2]

478 *Preparation of Metallic Molybdenum.*—Metallic molybdenum may be obtained as a grey powder which assumes a silver-white appearance under pressure by heating the trioxide or one of the chlorides in a current of hydrogen, but is best prepared by heating a mixture of molybdenum dioxide with one-tenth of its weight of sugar charcoal in a carbon crucible in the electric furnace, the action of the arc being stopped before the portions

[1] *Vetensk. Acad. Handl.*

[2] Heine, *J. pr. Chem.* 1836, **9**, 177.

in contact with the crucible have had time to fuse. It is thus obtained free from carbon, whereas if too strongly heated it takes up the latter in considerable quantities. The pure metal is as malleable as iron, and is not hard enough to scratch glass, has a specific gravity of 9·01, and can be forged when hot; it scarcely undergoes oxidation at the ordinary temperature, but is superficially attacked at a dull red heat, and rapidly at 600°, molybdenum trioxide subliming, and is rapidly attacked by fused potassium chlorate and nitrate. When coarsely powdered it is attacked by fluorine at the ordinary temperature, by chlorine at a dull red, and by bromine at a cherry-red heat, but not by iodine at the softening point of glass. It also combines with silicon and boron in the electric furnace, forming a crystalline silicide and boride.

It is insoluble in the dilute acids with the exception of nitric acid, but dissolves in concentrated sulphuric acid, the solution being first blue, but finally becoming colourless with formation of the trioxide, sulphur dioxide being also evolved.

MOLYBDENUM COMPOUNDS.

Molybdenum and Oxygen.

479 Molybdenum combines with oxygen to form a large number of oxides, many of which have a composition corresponding to those of chromium.

Molybdenum monoxide (hydrated), $MoO + xH_2O$.
Molybdenum sesquioxide, Mo_2O_3.
Molybdenum dioxide, MoO_2.
Molybdenum trioxide, MoO_3.

The first three are basic oxides, but very little is known of their salts other than the halogen derivatives. The trioxide is the most important, and like the analogous chromium oxide is an acid-forming oxide giving rise to the important series of *molybdates*; two other oxides, Mo_5O_{12} and Mo_3O_8, are formed by the combination of the basic oxides with the acidic trioxide. An oxide Mo_2O_5 and a peroxide Mo_2O_7 (?) have also been described.

Molybdenum monoxide, MoO, is obtained in the hydrated con-

dition as a black powder by boiling the dichloride with hot caustic potash.

Molybdenum Sesquioxide, Mo_2O_3, is formed when one of the higher oxides is treated with sodium amalgam, zinc, &c. When the trioxide is thus treated the colourless solution first becomes blue, then reddish-brown, and lastly black. The *hydroxide*, $Mo(OH)_3$, is obtained as a brownish-black precipitate by precipitating with ammonia, washing the precipitate with dilute ammonia, and drying in a current of hydrogen at 100°. When gently ignited in absence of air the water is evolved and the sesquioxide remains as a black mass (Berzelius). Molybdenum sesquioxide is likewise obtained in the form of a grey metallic powder by strongly igniting the trioxide in a current of hydrogen.[1] It is insoluble in acids, and even the hydroxide dissolves only with difficulty.

The Salts of the Sesquioxide are black or of a dark purple colour in concentrated solution, but when diluted they are transparent and of a purple tint. In the solid form the sesquisalts are dark-grey or black. They have a styptic taste, oxidise slightly on exposure to the air, are precipitated by alkalis with formation of the hydroxide, and give a brown precipitate with sulphide of ammonium soluble in excess of the reagent. Sulphuretted hydrogen also precipitates them, though slowly. Sodium phosphate produces a brownish-black precipitate.

Molybdenum Dioxide, MoO_2, is formed when the sesquioxide is gently heated in a current of air, or by igniting sodium trimolybdate for several hours in a current of hydrogen. It is obtained in dark-blue prisms resembling indigo by fusing the same salt with one-third of its weight of zinc, and extracting the mass alternately with caustic potash and hydrochloric acid;[2] this product, however, always contains a little admixed zinc molybdate, $Zn_2Mo_3O_8$, but it may be obtained pure by fusing together 8 grams of fused ammonium molybdate, 14 grams of potassium carbonate, and 7 grams of boron sesquioxide and extracting the cooled melt with water. It then forms opaque quadratic crystals, having a violet reflex, which are insoluble in boiling hydrochloric acid and caustic potash.[3]

Molybdic Tetrahydroxide, $Mo(OH)_4$, is obtained when a solution of the pentachloride or of ammonium molybdenum tetrachloride is precipitated with ammonia. On drying, the

[1] Svanberg and Struve, *Phil. Mag.* 1847 [3], **30**, 409.
[2] Ullik, *Annalen*, 1867, **144**, 227. [3] Muthmann, *Annalen*, 1887, **238**, 114.

precipitate has a dark-red colour; it dissolves slowly in water, yielding a yellow or dark-red solution which reddens litmus, has a somewhat acrid and metallic taste, and is precipitated on the addition of salts. In closed vessels it decomposes after some time, forming a transparent jelly. The ignited dioxide does not dissolve in aqueous acids, although the hydroxide does so.

The Salts of the Dioxide are very unstable, and are formed when an excess of molybdenum is treated with the corresponding acid, and then the requisite quantity of nitric acid added. The concentrated solutions are black, and on dilution they become of a bluish-green, greenish-yellow, dark-red, and lastly yellow colour. On exposure to the air they absorb oxygen and become blue, whilst with zinc they give a black precipitate of $Mo(OH)_3$. With alkalis they yield a reddish-brown precipitate, and with sulphuretted hydrogen, and sulphide of ammonium, give the same reactions as the salts of the sesquioxide.

Molybdenum Trioxide and Molybdic Acid.

480 *Molybdenum Trioxide*, MoO_3, occurs as molybdic ochre in crystalline or fibrous masses, as well as in the form of an earthy powder or incrustation. It is usually found with molybdenite, and has probably been formed by its oxidation.

In order to prepare the trioxide in the pure state on the small scale the native sulphide may be heated in a combustion tube in a current of air until it is all oxidised, and the trioxide sublimed.[1] On the larger scale it may be obtained by mixing the same powdered mineral with an equal weight of pure quartz sand and roasting the mixture on a flat iron plate. The roasted product is then boiled with dilute ammonia, and a small quantity of sulphide of ammonium added to the solution in order to precipitate the copper. The filtered liquid is then evaporated to dryness, and the residue again dissolved in dilute ammonia. Crystals of ammonium molybdate are obtained from the filtrate on concentration. These are decomposed by nitric acid, evaporated to dryness, and the residual trioxide well washed with water. Molybdenum trioxide can also be obtained from native lead molybdate by first treating the mineral with dilute hydrochloric acid in order to remove iron, zinc, &c., then decomposing it with hot concentrated hydrochloric acid, evaporating down

[1] Wöhler, *Annalen*, 1856, **100**, 376.

and digesting with dilute ammonia, when ammonium molybdate remains in solution and can be crystallised out as already described.[1] The ammonium molybdate may also be converted into the trioxide by igniting in a platinum dish and subsequently heating to a dull-red heat in a current of oxygen.[2]

Molybdenum trioxide is a white impalpable powder, which when heated becomes yellow; it melts at a red-heat to a dark yellow liquid, which, on cooling, solidifies to a yellowish-white fibrous crystalline mass, having a specific gravity of 4·39 (Schafarik). It volatilises at very high temperatures when heated in closed vessels, but in the air it sublimes more easily, depositing small colourless transparent rhombic tablets. It dissolves in 500 parts of cold, and in about 960 parts of hot water. The solution reddens litmus paper, turns turmeric paper brown, and possesses a sharp metallic taste.

Molybdic Acid, $H_2MoO_4 + H_2O$, crystallises out in yellow crusts when a solution of three parts of ammonium molybdate is dissolved in twenty parts of water, and the same quantity of nitric acid of specific gravity 1·16 is added to the solution and the whole allowed to stand. The deposition of the acid frequently takes place only very slowly, and the addition of a crystal of the compound renders its separation more easy.[3]

When the solution of the trioxide in nitric acid is allowed to evaporate spontaneously a white crystalline powder separates, which on heating loses water (Berzelius). This probably consists of the anhydrous acid, H_2MoO_4, which was once obtained by Ullik in the form of thin prismatic crystals by the decomposition of magnesium molybdate with nitric acid.

Colloidal Molybdic Acid.—When the hydrochloric acid solution of ammonium molybdate is dialysed, a yellow, strongly acid, astringent solution of molybdic acid remains, which on evaporation yields a deliquescent gummy mass.[4] After drying over sulphuric acid for several weeks it has the empirical formula $H_2Mo_2O_7$, but the determination of the molecular weight by Raoult's method indicates that it contains four MoO_3 groups.[5] If ordinary ammonium molybdate be precipitated with barium chloride, and the washed precipitate decomposed with the exact

[1] Wöhler, *Mineralanalyse*, 146.
[2] Muthmann, *Annalen*, 1887, **238**, 117.
[3] Gmelin-Kraut, **2**, 171.
[4] Graham, *Journ. Chem. Soc.* 1864, 326.
[5] Sabanéef, *Journ. Chem. Soc.* 1890, ii. 1215.

quantity of sulphuric acid, a colourless solution is obtained, possessing an acid reaction and metallic taste. When dried over sulphuric acid for several months it has the composition $H_2Mo_2O_7$, and on heating at 100°, 120°, and 160—170°, the residues have the composition $H_2Mo_2O_7$, $H_2Mo_4O_{13}$, and $H_2Mo_8O_{25}$ respectively; at 250° pure molybdenum trioxide remains behind.

Molybdenum trioxide generally behaves as an acid forming oxide analogous to chromium trioxide, and unites with bases to form molybdates. The normal molybdates are unstable, and show a great tendency to form polymolybdates corresponding to the polychromates by uniting with further molecules of the trioxide, as many as ten molecules of MoO_3 combining with one equivalent of a basic oxide.

The molybdates also combine with other acidic oxides forming the series of salts known under the general term of the complex molybdates. The best known of these are the phosphomolybdic acids, in which a varying number of molecules of molybdenum trioxide and of phosphoric anhydride are combined with a basic oxide (p. 861); similar compounds are formed by the acidic oxides of arsenic, vanadium, antimony, and also of iodine, tin and silicon. The exact constitution of these salts is not yet known.

Molybdenum trioxide acts towards strong acids as a basic oxide; thus it combines with two molecules of hydrochloric acid to form a volatile crystalline compound, which is probably the *hydroxychloride*, $MoO(OH)_2Cl_2$; with sulphuric acid it yields the compound $MoSO_6$, which is the sulphate of the radical molybdenyl, MoO_2SO_4, analogous with the salts formed by tungsten and uranium trioxides.

Sodium Molybdates.—The normal molybdate, Na_2MoO_4, is formed by fusing the trioxide with the requisite quantity of sodium carbonate, and crystallises from water in acute rhombohedra, containing 2 molecules of water; below 6° prisms containing 10 molecules of water separate out, resembling Glauber's salt in appearance, which effloresce in the air forming the first-named salt. The *dimolybdate*, $Na_2Mo_2O_7$, is formed when sodium carbonate and the trioxide are fused in the requisite proportions, and is a crystalline mass soluble with difficulty in cold and only slowly in hot water. The *trimolybdate*, $Na_2Mo_3O_{10}+7H_2O$, obtained in a similar manner, crystallises in large needles, 3·878 parts of which dissolve in 100 parts of water at 20° and in 137

parts at 100°. The *tetramolybdate*, $Na_2Mo_4O_{13}+11H_2O$, is prepared by the action of the calculated quantity of hydrochloric acid on the normal salt and forms small glistening crystals soluble with difficulty in cold, but readily in hot water. An excess of hydrochloric acid gives rise to the acid salt, $NaHMo_4O_{13}+8H_2O$, which forms long efflorescent monosymmetric crystals readily soluble in water. *Sodium Octomolybdate*, $Na_2Mo_8O_{25}+4H_2O$, is formed as a white powder by the action of a solution of sodium carbonate on the acid salt $HNaMo_8O_{25}+4H_2O$, which latter salt is obtained by boiling the normal sodium molybdate with nitric acid, and also forms a white or yellowish powder. The *Decamolybdate*, $Na_2Mo_{10}O_{31}+12H_2O$, is a white crystalline powder obtained by heating the normal salt on the water-bath with sufficient hydrochloric acid to saturate the requisite quantity of sodium. It is difficultly soluble in water. If soluble molybdic acid be dissolved in the requisite quantity of sodium carbonate, the salt $Na_2Mo_{10}O_{31}+21H_2O$, crystallises in monosymmetric prisms, and is soluble in cold water without decomposition.

A salt containing 3 equivalents of soda to 7 of molybdenum trioxide is obtained by allowing a solution of the calculated quantity of the trioxide in sodium carbonate to evaporate spontaneously, the crystals having the composition $Na_6Mo_7O_{24}+22H_2O$. On heating it loses water and yields the anhydrous salt, which solidifies in long needles readily soluble in water.

Potassium Molybdates.—The normal salt, K_2MoO_4, obtained in a similar manner to the sodium salt, crystallises in microscopic four-sided crystals, which are readily soluble in water. When hydrochloric acid is added drop by drop to a solution of the trioxide in potassium carbonate until a permanent turbidity is produced, a salt of the composition $K_6Mo_7O_{24}+4H_2O$ separates out, on standing, in monosymmetric prisms, which are decomposed by water into the *trimolybdate* $K_2Mo_3O_{10}+3H_2O$, which forms silky pliable needles. If this is dissolved in molybdic acid prepared from ammonium molybdate, a crystalline precipitate is formed which dissolves in hot water and on cooling deposits glistening crystals of the *tetramolybdate*, $K_2Mo_4O_{13}+6H_2O$.

Ammonium Molybdates.—The *normal molybdate*, $(NH_4)_2MoO_4$, is produced when molybdenum trioxide or an ammonium polymolybdate is heated with excess of concentrated ammonia, and crystallises in four-sided prisms which are decomposed by water. When a solution of the trioxide in ammonia is evaporated, the

compound $(NH_4)_6Mo_7O_{24}+4H_2O$ crystallises out in large colourless monosymmetric crystals. This is the salt usually known as ammonium molybdate. The *Dimolybdate*, $(NH_4)_2Mo_2O_7$, separates out on evaporating the mother-liquor of the normal salt in the form of a white crystalline powder. The *Trimolybdate*, $(NH_4)_2Mo_3O_{10}+H_2O$, is frequently formed by the decomposition of a solution of the ordinary salt at a low temperature, when it separates out in silky needles difficultly soluble in cold, but readily so in hot water.

Calcium Molybdate, $CaMoO_4$, is obtained by precipitating a solution of the ordinary ammonium salt containing an excess of ammonia with calcium chloride. It forms a white precipitate consisting of microscopic quadratic pyramids. If calcium carbonate be boiled with an excess of the trioxide and water, and the solution allowed to evaporate spontaneously, *calcium trimolybdate*, $CaMo_3O_{10}+6H_2O$, is deposited. The salt $H_2CaMo_8O_{26}+17H_2O$ crystallises from a solution of the normal salt in the requisite quantity of hydrochloric acid. It is deposited in small oblique glistening prisms which are scarcely soluble in cold but readily dissolve in hot water.

Barium Molybdate, $BaMoO_4$, is a crystalline precipitate difficultly soluble in acids. It is obtained in quadratic pyramids by fusing together sodium molybdate, barium chloride, and common salt.

When the ordinary ammonium salt is precipitated with barium chloride a flocculent precipitate of $Ba_3Mo_7O_{24}+9H_2O$ is thrown down, which is slightly soluble in water. A compound, $BaMo_3O_{10}+3H_2O$, having properties similar to the last salt, is obtained by precipitating a soluble trimolybdate. When barium carbonate is dissolved in soluble molybdic acid and the solution allowed to stand, oblique prisms of the salt $H_2BaMo_8O_{26}+17H_2O$ are deposited; and if the normal salt be treated with dilute nitric acid the compound $BaMo_9O_{28}+4H_2O$ is formed. This is insoluble in water and is not completely decomposed by acids, not even by sulphuric acid.

Magnesium Molybdate, $MgMoO_4+5H_2O$, is obtained by boiling magnesia with water and molybdenum trioxide, and evaporating the solution, when the salt separates out in long glistening transparent prisms. Magnesium molybdate forms with the molybdates of potassium and sodium double salts such as $K_2MoO_4+MgMoO_4+2H_2O$, which appear to be isomorphous with the corresponding manganese and ferrous salts.

Lead Molybdate, $PbMoO_4$.—This occurs native as wulfenite in orange-red transparent quadratic tables and octohedra, which have a specific gravity varying from 6 to 7. When one part of sodium molybdate is fused with six parts of lead chloride and four of sodium chloride in a closed crucible, bright-yellow translucent pyramids or tables of the artificial compound are obtained, which have a specific gravity of 6·811. If a solution of a molybdate be added to lead nitrate the same compound is also obtained in the form of a white precipitate which melts at a very high temperature. We are not acquainted with any other lead molybdate.

Molybdenum Molybdates.—When ammonium molybdate is fused with two parts of molybdenum trioxide for a few minutes, and the melt extracted first with ammonia, and then with hydrochloric acid, the compound $Mo_5O_{12} = 3MoO_2.2MoO_3$ remains as a lustrous violet powder or copper coloured plates, and is volatile at a dark red heat. It is dissolved by concentrated sulphuric acid forming a green solution which is also obtained by the action of the acid on molybdenum. When all the molybdenum is dissolved the solution becomes first blue, owing to the formation of the higher oxide Mo_3O_8, which is probably also a molybdenum molybdate, and finally becomes colourless with formation of the trioxide. The blue oxide is also obtained in solution by the reduction of molybdic acid by sulphuretted hydrogen, sulphur dioxide, stannous chloride, &c., the formation of this blue solution forming one of the most characteristic tests for molybdenum. The oxide Mo_3O_8 forms a blue precipitate, which contains water, and is sparingly soluble even after drying.

When the first-named blue oxide is heated in the air, it is converted, according to Wöhler and Buff into another blue oxide, $Mo_2O_5 = MoO_2 + MoO_3$, and a hydrated oxide, $2Mo_2O_5 + 3H_2O$, is obtained according to Smith and Oberholzer[1] by heating molybdic acid in a current of hydrogen at 105–120°.

481 *Phosphomolybdic Acid*, $H_3PO_4 + 12MoO_3$.—This complex acid is obtained by the repeated treatment of the ammonium salt with small quantities of aqua regia, and crystallises out on evaporation of the combined solutions. It forms at least three different crystalline hydrates, but the statements of different authors as to the number of molecules of water in these vary

[1] *Zeit. anorg. Chem.* 1893, **4**, 236.

considerably. Debray[1] gives 21, 38, and 48 molecules to one of P_2O_5, Gibbs[2] 27, 46, and 59 molecules, and Finkener[3] 29 and 58 molecules. Debray also believed that the ratio of P_2O_5: MoO_3 was 1 : 20, but Gibbs and Finkener have shown that it is 1 : 24.

Ammonium Phosphomolybdate, $(NH_4)_3PO_4+12MoO_3$.—This salt was discovered by Gmelin,[4] but Sonnenschein[5] was the first to notice that this compound contained phosphoric acid as an essential constituent. It is formed when a solution of a molybdate is mixed with ammonia, and a small quantity of phosphoric acid in nitric acid solution added, or when the free acid is added to a strongly acid solution of the ammonium salt. Under these circumstances a canary-coloured yellow powder is thrown down. Pyro- and meta-phosphates do not yield this precipitate; it is only formed when they are converted into orthophosphates. When this change takes place slowly the compound is obtained in glistening yellow crystals (Debray). It is almost insoluble in water and in dilute acids and is also insoluble in a nitric acid solution of ammonium molybdate. The presence of hydrochloric acid and chlorides, as well as of many organic acids, with the exception of acetic acid, retards the formation, whilst in presence of an excess of phosphoric acid no precipitation occurs.

When dried at above 130° it always has the composition given above, in which the ratio P_2O_5: MoO_3 is 1 : 24, but according to Gibbs the hydrated precipitate has the composition $(NH_4)_3PO_4,12MoO_3+(NH_4)_2HPO_4,11MoO_3+8H_2O$. It dissolves in 10,000 parts of pure water, in 6,600 parts of one per cent. nitric acid, and in 550 parts of hydrochloric acid of specific gravity 1·12. It is readily soluble in alkalis, and on allowing the ammoniacal solution to remain, glistening needles or prisms having the composition $2(NH_4)_3PO_4+5MoO_3+7H_2O$ separate out. These are sparingly soluble in cold, readily in hot water, forming a slightly acid liquid.

Phosphomolybdic acid also precipitates strongly acid solutions of the salts of rubidium, cæsium, thallium, and the organic alkaloids, but not solutions of sodium or lithium salts. The heavy metals are also not precipitated if a sufficient amount of free acid be present. This acid is used as a reagent for the alkaloids

[1] Debray, *Compt. Rend.* 1868, **66**, 700.
[2] *Amer. Chem. Journ.* 1881—2, **3**, 317.
[3] *Ber.* 1878, **11**, 1638.
[4] *Handbook*, vol. iv. 68.
[5] *J. pr. Chem.* **53**, 342.

or, in place of this, a liquid prepared by saturating a solution of sodium carbonate with molybdenum trioxide, and adding one part of sodium phosphate to every part of the trioxide, may be employed; this solution is evaporated to dryness, the residue fused, dissolved in water, filtered, and nitric acid added until the liquid becomes yellow.

In addition to these salts, others have been prepared in which the ratio P_2O_5: MoO_3 is 1: 15–18, and it appears not improbable that some exist in which the ratio is even higher than 1: 24. Arsenic acid gives rise to an analogous series of complex acids, in the highest of which the ratio As_2O_5: MoO_3 appears to be 1: 20.

Permolybdic Acid.—The molybdates when treated with hydrogen dioxide in acid solution give a yellow coloration, but the yellow substance cannot be extracted by ether. If molybdic acid be allowed to evaporate in a vacuum with hydrogen dioxide a yellow amorphous insoluble mass remains. Potassium trimolybdate dissolves in hydrogen dioxide yielding an orange-yellow solution, which on concentration at a moderate heat, yields yellow crystals of *potassium permolybdate*, $KMoO_4 + 2H_2O$. When gently heated in a vacuum, these lose water and oxygen, leaving a residue of potassium dimolybdate.[1]

Molybdenum and the Halogens.

482 No fluoride of molybdenum has been isolated, but double salts of molybdenum oxytrifluoride with other fluorides are known, most of which are well crystallised substances. *Molybdyl fluoride*, MoO_2F_2, is a derivative of molybdic acid, analogous to chromyl fluoride and also yields crystalline double salts.

Molybdenum Dichloride, $(MoCl_2)_x$, is prepared by heating the trichloride in a current of dry carbon dioxide, $2MoCl_3 = MoCl_2 + MoCl_4$. The tetrachloride volatilises, leaving the dichloride as a sulphur-yellow amorphous powder, which does not alter in contact with the air, does not dissolve in water and is soluble in alcohol and ether, separating from these solutions in the amorphous condition.[2] It is also soluble in the hydracids and in hot sulphuric acid, and in the alkalis, from which latter solution the monoxide

[1] Péchard, *Compt. Rend.* 1891 **112**, 720.
[2] Liechti and Kempe, *Annalen*, 1873, **169**, 351.

separates on boiling. The hydrate, $MoCl_2 + H_2O$, crystallises from the hydrochloric acid solution, on standing, in pale-yellow plates insoluble in water, but when the solution is evaporated long prisms having the formula $MoCl_2 + 2H_2O$ are deposited. These are soluble in water and when dissolved in hot hydrochloric acid long glittering needles of the compound, $MoCl_2 + 3H_2O$, are deposited. These do not dissolve in water, but are decomposed by it with evolution of hydrochloric acid.

Molybdenum Dibromide, $MoBr_2$, is formed by the decomposition of the tribromide by heat. It forms a yellowish-red infusible mass which does not dissolve in water or in acids.

The molecular formulæ of these two compounds are probably treble those which are here given, for if the chloride be dissolved in caustic potash the compound $Mo_3Cl_4(OH)_2 + 2H_2O$ is thrown down on the addition of acetic acid in the form of a pale yellow amorphous precipitate. This compound, which has been termed *chloromolybdic hydroxide*, possesses basic properties, and forms with acids well-defined salts.[1]

Chloromolybdic Bromide, $Mo_3Cl_4Br_2 + 3H_2O$, is obtained by heating the hydroxide or the chloride with hydrobromic acid. It crystallises on cooling in glittering reddish-yellow plates which scarcely dissolve in water or in dilute hydrochloric acid. If the mother-liquor of this salt be evaporated well-formed reddish-yellow prisms having the composition $Mo_3Cl_4Br_2 + 6H_2O$ are deposited. These dissolve in water, but are decomposed with separation of a yellow granular powder. Hydriodic acid forms corresponding compounds.

Bromomolybdic Hydroxide, $Mo_3Br_4(OH)_2 + 8H_2O$.—When molybdenum dibromide is dissolved in dilute alkali and the solution allowed to stand exposed to the air, or when ammonium chloride is added to the hot solution, the above compound is deposited in the form of golden-yellow glistening rhombohedral closely approximating in form to the cube. These lose six molecules of water on drying over sulphuric acid, and assume a dark-red colour. At 100° they lose all their water, a fine red powder remaining behind.[2]

Bromomolybdic Fluoride, $Mo_3Br_4F_2$, is prepared with hydrofluoric acid in the same way as the chloride, which it closely resembles.

Bromomolybdic Chloride, $Mo_3Br_4Cl_2 + 3H_2O$, is obtained as a

[1] Blomstrand, *J. pr. Chem.* 1859, **77**, 100.
[2] Atterberg, *Ber.* 1873, **6**, 1464.

pale-yellow powder on adding an excess of hydrochloric acid to the alkaline solution of the hydroxide.

Bromomolybdic Sulphate, $Mo_3Br_4SO_4+3H_2O$, can be obtained in the same way in the form of a yellow precipitate, whilst when the solution of the hydroxide is treated with ammonium molybdate and acetic acid, *bromomolybdic molybdate*, $Mo_3Br_4MoO_4+H_2O$, is thrown down as a reddish-yellow precipitate.

Molybdenum Trichloride, $MoCl_3$, is formed when the pure pentachloride is volatilised in a current of carbon dioxide, the tube being heated strongly at one point only. The trichloride is deposited as a copper-red crystalline crust.[1] If the pentachloride be heated in a current of hydrogen to 250° the trichloride is also obtained in a form closely resembling red phosphorus (Liechti and Kempe). Heated in the air it forms a white woolly sublimate, whilst impure dichloride remains behind. It is insoluble in cold water and is decomposed by boiling water. It likewise does not dissolve in hydrochloric acid, though it is easily soluble in hot nitric acid, whilst sulphuric acid dissolves it with a blue colour which on heating becomes green. If the hydroxide be dissolved in hydrochloric acid a brown liquid is obtained which on evaporation dries to a black pitch-like mass.

Molybdenum Tribromide, $MoBr_3$, is formed by the action of bromine vapour on the heated metal. It sublimes in a mass of fine blackish-green needles which are insoluble in water though soluble in cold dilute nitric and in boiling hydrochloric acid. On boiling with alkalis the hydroxide is formed (Blomstrand).

Molybdenum Tetrachloride, $MoCl_4$, is obtained together with the dichloride, as has been stated, by heating the trichloride in an atmosphere of carbon dioxide. The tetrachloride volatilises as a dark yellow vapour which condenses to a brown crystalline powder. When exposed to the air it becomes of a bluish-green colour and deliquesces to a brown liquid. It is only slowly soluble in hydrochloric acid, and dissolves in concentrated sulphuric acid with a bluish-green colour.

Molybdenum Tetrabromide, $MoBr_4$, is formed in small quantities in the preparation of the tribromide as black glistening needles, which fuse when heated, volatilising in brownish-red vapours. These readily decompose into bromine and dibromide, and in presence of air the compound deliquesces, forming a dark liquid giving with more water a yellowish-brown solution.

Molybdenum Tetriodide, MoI_4.—The hydroxide dissolves in

[1] Blomstrand, *J. Pr. Chem.* 1859, **77**, 96.

hydriodic acid, giving a red-coloured solution, which on spontaneous evaporation yields crystals which transmit red light and appear brown by reflected light.

Molybdenum Pentachloride, $MoCl_5$.—This, the highest chloride of molybdenum, is formed by heating molybdenum or molybdenite in dry chlorine for some time, when bright metallic glistening black crystals are formed which melt at 194° and boil at 268°, giving a dark-red vapour which has a specific gravity of 9·4 to 9·53 [1] corresponding to the above formula. The compound fumes on exposure to moist air and becomes of a bluish-green colour, gradually deliquescing to a brown liquid which on dilution with water becomes colourless. Absolute alcohol and ether yield green solutions, and the chloride also dissolves in hydrochloric acid with evolution of heat.

When molybdenum trioxide is heated with phosphorus pentachloride to 170° the compound, $MoCl_5 + POCl_3$, is formed. It crystallises in dark green prisms, and when heated the compound decomposes into its two constituents.

Oxy-Haloid Derivatives of Molybdenum.

483 Molybdenum forms a large number of derivatives containing oxygen and the halogens, many of which are volatile and crystalline and yield crystalline double salts with other metallic haloids.

Molybdenyl Fluoride, MoO_2F_2, is obtained by heating the trioxide with cryolite or lead fluoride as an amorphous sublimate having a bluish tinge, which decomposes in the air into hydrofluoric acid and molybdenum trioxide [2]; it is obtained in solution by dissolving the trioxide in hydrofluoric acid. Crystalline double salts are formed by dissolving the normal and polymolybdates in hydrofluoric acid.

Potassium Molybdic Oxyfluoride, $K_2MoO_2F_4 + H_2O = MoO_2F_2, 2KF + H_2O$, forms small asymmetric crystals, and the acid salt $K_2(F_3MoO_2)_2 + 2H_2O (= MoO_2F_2, KF + H_2O)$ crystallises in silky needles which evolve hydrofluoric acid on exposure to air.[3]

Molybdenum Oxytetrachloride, $MoOCl_4$, is formed by the action of chlorine on a moderately-heated mixture of carbon and

[1] Debray, *Compt. Rend.* 1868, **66**, 732.
[2] Schultze, *J. Pr. Chem.* 1880, **21**, 442.
[3] Delafontaine, *Arch. Sc. Phys. Nat.* 1855, **30**, 240.

molybdenum dioxide. It forms a dark-green crystalline mass, or, if obtained at a higher temperature, light-green plates having a metallic lustre. It melts and evaporates below 100°, solidifying to a green glistening mass and yielding a dark-red vapour. It is readily decomposed by water, deliquescing in moist air to a blue liquid, and this on addition of water gives a blue precipitate which becomes brown in presence of ammonia.

Molybdenyl Chloride, MoO_2Cl_2.—This compound was originally supposed to be the hexachloride, its true composition being first ascertained by Rose. It is obtained by heating the dioxide in chlorine and also together with other chlorides, when a mixture of the trioxide and carbon is substituted for the dioxide. It sublimes usually as an amorphous mass, and only melts in closed vessels, in which it may be sublimed at low temperatures yielding thin quadratic plates, or mossy aggregates. It dissolves readily in water and alcohol.

Molybdenum Trioxypentachloride, $Mo_2O_3Cl_5$, is frequently formed in the preparation of molybdenum chlorides from materials containing oxygen, and is best obtained by heating the trioxide in chlorine; when carefully sublimed in a current of hydrogen it yields well-developed dark reddish brown crystals, which may be readily melted and volatilised, and dissolve in water forming a solution which is first colourless, then green and finally blue.

Another oxychloride, $Mo_2O_3Cl_6$, is obtained by the repeated sublimation of the oxytetrachloride, and forms well developed violet prisms, which are decomposed on heating in the air into molybdenyl chloride and chlorine. When heated to a temperature somewhat higher than that needed for its formation it yields $Mo_3O_5Cl_8$, which forms pale red needles and is stable in the air. Püttbach has prepared several other oxychlorides.[1]

Molybdenyl Hydroxychloride, $MoO(OH)_2Cl_2$, is obtained by the action of hydrogen chloride on the trioxide at 150–200°, and is a white crystalline substance which is only volatile without decomposition in an atmosphere of hydrogen chloride.[2]

Molybdenyl Bromide, MoO_2Br_2, is formed when bromine vapour is passed over the heated dioxide, or when a mixture of molybdenum trioxide and boron trioxide is heated with bromide of potassium :—

$$MoO_3 + B_2O_3 + 2KBr = MoO_2Br_2 + 2KBO_2.$$

It forms yellow tablets which deliquesce on exposure to air.

[1] *Annalen*, 1880, **201**, 23. [2] Debray, *Compt. Rend.* 1858, **46**, 1101.

Molybdenum and Sulphur.

484 *Molybdenum Disulphide*, MoS_2, is found native as molybdenite in Sweden, Norway, Bohemia, Saxony, the Urals, at Caldbeck Fells in Cumberland, in Connecticut, California, and elsewhere. It commonly occurs in foliated masses or in scales, and sometimes in tabular hexagonal prisms, and in its general appearance is very similar to graphite, since it possesses a metallic lustre and pure lead-grey colour, and leaves a greenish-grey trace on paper. Molybdenite generally occurs embedded in or disseminated through granite, gneiss, zirconsyenite, granular limestone, and other crystalline rocks.

When the trioxide is fused with sulphur, or heated in a current of sulphuretted hydrogen, the same compound is obtained in the form of a glistening black powder, easily distinguished from graphite by the facts that when heated before the blowpipe it is incombustible, that it oxidises when heated in the air with evolution of sulphur dioxide, and formation of molybdenum trioxide, and that it is readily oxidised by nitric acid and aqua-regia.

Molybdenum Trisulphide, MoS_3, is formed when sulphuretted hydrogen is passed into the concentrated solution of a molybdate, and hydrochloric acid added to the liquid. It may likewise be prepared by boiling the molybdate of an alkali metal for a short time with sulphide of ammonium, and then precipitating with dilute sulphuric acid. Thus obtained it is a reddish-brown precipitate which dries to a blackish-brown powder. On heating in absence of air it splits up into the foregoing compound and sulphur. It combines with basic sulphides to form thio-salts.

Potassium Thiomolybdate, K_2MoS_4, is formed when potassium molybdate is saturated with sulphuretted hydrogen. On evaporating the solution the compound crystallises out in ruby-red four- or eight-sided tablets which have a green metallic lustre, and dissolve in water with a yellowish-red colour.

Ammonium Thiomolybdate, $(NH_4)_2MoS_4$, is obtained by dissolving the trisulphide in ammonium sulphide, and crystallises in cinnabar-red scales.

A series of complicated mono- and di-thiomolybdates has been described by Krüss.

Molybdenum Tetrasulphide, MoS_4, is prepared by heating pentathiomolybdic acid to 140° as a cinnamon brown powder which undergoes slight oxidation in the air. The latter is obtained

as a reddish brown powder by the action of dilute hydrochloric acid on the potassium salt.

Potassium Pentathiomolybdate, $KHMoS_5$, is obtained by evaporating a solution of potassium dimolybdate which has been saturated with sulphuretted hydrogen, and separates in blood-red prisms probably belonging to the rhombic system, which are sparingly soluble in water. A black powder consisting of molybdenum di- and trisulphides separates out at the same time.[1]

Perthiomolybdic Acid, $HMoS_6$.—When a solution of normal ammonium thiomolybdate is mixed with a solution of ammonium polysulphides, *ammonium hexathiomolybdate* or *perthiomolybdate* separates out in black lustrous needles, which are sparingly soluble in water and alcohol. By the action of caustic potash it yields the corresponding potassium salt, $KMoS_6$, which crystallises in thin dark brown plates, and is more soluble in water than the ammonium salt. The free acid $HMoS_6$ is obtained by treating the ammonium salt with cold 10 per cent. hydrochloric acid and washing the product with carbon bisulphide.[2]

Molybdenum and Phosphorus.

Molybdenum Phosphide, MoP, is obtained by strongly heating molybdenum trioxide and metaphosphoric acid in a carbon crucible. It forms a grey vesicular mass having a metallic lustre and containing crystals in the cavities. On ignition in the air it oxidises slowly, and takes fire when thrown into fused nitre.

Detection and Estimation of Molybdenum.

485 Molybdenum trioxide and the molybdates may be detected inasmuch as the colourless hydrochloric acid solution when brought into contact with zinc becomes of a blue, green, and lastly dark-brown colour. The lower oxides, as well as their salts, can be readily transformed into the molybdates by oxidation. Molybdenum trioxide colours the blowpipe flame a yellowish green, and imparts to a bead of borax or microcosmic salt, a fine green colour in the reducing flame. Hydrochloric or nitric acid produces a curdy precipitate in solutions of a molybdate when not too dilute. This dissolves in an excess of acid, and even

[1] *Annalen*, 1884, **225**, 1. [2] Hofmann, *Zeit. anorg. Chem.* 1896, **12**, 55.

in a large quantity of water. A solution of ammonium molybdate in nitric acid becomes yellow-coloured on the addition of a few drops of sodium phosphate, and on warming a heavy yellow precipitate of ammonium phosphomolybdate (p. 862) separates out. If some zinc be added even to a very dilute solution of a molybdate, and then hydrochloric acid, and a concentrated solution of potassium thiocyanate, the liquid becomes of a deep red colour, the red compound being extracted on shaking up with ether.

Molybdenum trisulphide is slowly precipitated from an acid solution by sulphuretted hydrogen, and it dissolves readily in ammonium sulphide. When the solution containing ammonium thiomolybdate is acidified with dilute nitric acid, molybdenum trisulphide is thrown down.

In order to estimate molybdenum *quantitatively* it must be obtained as a neutral molybdate, which is then precipitated with a neutral solution of mercurous nitrate. The yellow precipitate which falls down is washed with a solution of mercurous nitrate, dried, and then either heated in a stream of hydrogen, when molybdenum dioxide is formed, or ignited with a weighed quantity of anhydrous lead oxide until all the mercury is driven off. The increase of weight then gives the amount of trioxide present.

486 *Atomic Weight of Molybdenum.*—The determination of the atomic weight of molybdenum has been frequently made, but with very varying results. Berzelius found the number 94·9, but Svanberg and Struve obtained the number 92·5, which was confirmed by Berlin, and then generally adopted. The investigation of Dumas[1] then showed that the number of Berzelius was much more nearly correct, the average obtained by the reduction of the trioxide to the metal in a current of hydrogen being 95·3; the numbers in the different experiments varying, however, from 94·7 to 95·6. Debray[2] obtained the number 94·8 by the same method, whilst Liechti and Kampe[3] by the analysis of the di-, tri-, and pentachloride of molybdenum obtained the same average number as Dumas; but in this case also the numbers found in the different experiments varied considerably. More recently Smith and Maas[4] have found the number 95·37, the method

[1] *Ann. Chim. Phys.* 1859 (3), **55**, 129.
[2] *Compt. Rend.* 1868, **66**, 732.
[3] *Annalen*, 1873, **169**, 360.
[4] *Zeit. anorg. Chem.* 1893, **5**, 280.

adopted being to heat pure sodium molybdate in a current of hydrogen chloride, when the following reaction takes place:—

$$Na_2MoO_4 + 4HCl = 2NaCl + Mo(OH)_2OCl_2 + H_2O.$$

The last two being volatile, only pure sodium chloride remains behind, and from the amount of this obtained from a given quantity of sodium molybdate, the above number was obtained as the average of ten closely agreeing experiments. Lastly, Seubert and Pollard,[1] by the acidimetric determination of molybdic acid, obtained the number 95·25, and by the reduction of the trioxide to the metal in a current of hydrogen the number 95·31 (O = 15·88). The atomic weight may therefore be taken as 95·3.

TUNGSTEN, W = 182·7.

487 The minerals tungsten or heavy-stone, now termed scheelite or calcium tungstate, and wolfram (the *lupi spuma* of Agricola) were, up to the middle of the eighteenth century, both classed amongst the tin ores. In 1781, Scheele proved that tungsten was composed of lime combined with a peculiar acid, and in the same year, Bergman stated that, in his opinion, this acid was a metallic calx. Two years later the Spanish chemists Juan, José, and Fausto d'Elhujar,[2] showed that this same acid is contained in the mineral wolfram combined with iron and manganese. They also succeeded in producing metallic tungsten from the acid.

Tungsten is not a common metal, being found only in a few minerals, some of which occur, however, in fairly large quantities. The most important of these is wolfram, a tungstate of iron and manganese found in Cornwall, in Cumberland, on Rona in the Hebrides, in County Wicklow, at Zinnwald, and in many localities in the United States. Other important tungsten minerals are scheelite or calcium tungstate, $CaWO_4$, and scheelitine or lead tungstate, $PbWO_4$. In addition to these, tungsten occurs in the following somewhat rare minerals: wolfram

[1] *Zeit. anorg. Chem.* 1895, **8**, 434.

[2] *A Chemical Analysis of Wolfram and Examination of a New Metal, which enters into its Composition.* Translated from the Spanish by C. Cullen, to which is prefixed a translation of Mr. Scheele's analysis of the Tungsten, or heavy-stone, with Mr. Bergman's supplemental remarks. London, 1785.

ochre, WO_3; wolframite, $(Mn,Fe)WO_4$; ferberite, $FeWO_4$; hübnerite, $MnWO_4$; and cupro-scheelite, $(Ca,Cu)WO_4$.

In order to obtain the tungsten compounds from wolfram, a process proposed by Oxland in 1848 (see Tin), is generally adopted, the ore being fused with soda ash and sodium nitrate in a reverberatory furnace, and the soluble sodium tungstate dissolved out and obtained by crystallisation.

Metallic Tungsten may be obtained by the reduction of the trioxide with carbon or in a current of hydrogen, or by the reduction of the chloride in the vapour of sodium. It is best prepared by heating a mixture of the trioxide with one-tenth of its weight of sugar charcoal in the electric furnace, and if care be taken that complete fusion of the metal does not occur, the latter is free from carbon. The metal thus obtained is as a rule fused on the surface, but is porous internally, and can be welded like iron.[1] It has a bright grey lustre, a higher melting point than chromium and molybdenum, a specific gravity of 19·129 (Roscoe),[2] 18·7 (Moissan), and a specific heat of 0·0338,[3] and when free from carbon will not scratch glass. It is attacked by fluorine at the ordinary temperature with incandescence, by chlorine at 250—300°, but has no action on nitrogen and phosphorus at a red heat; when heated with carbon, silicon or boron in the electric furnace it yields crystalline compounds having a metallic lustre, which are hard enough to scratch rubies. At a red heat the powdered metal burns in air forming the trioxide, but it is not readily oxidised by moist air, although it is slowly attacked by water containing carbon dioxide, and is readily oxidised when heated with oxidising agents such as lead dioxide or potassium chlorate. Sulphuric, hydrochloric, and hydrofluoric acids act upon it slowly, but it is readily dissolved by a mixture of nitric and hydrofluoric acids, and the powdered metal is rapidly oxidised by aqua regia, and dissolves in boiling caustic potash solution with formation of potassium tungstate and evolution of hydrogen.

[1] Moissan, *Compt. Rend.* 1896, **123**, 13.
[2] *Mem. Manch. Lit. and Phil. Soc.* 1872, [3], **5**, 77.
[3] Grodspeed and Smith, *Zeit. anorg. Chem.* 1895, **8**, 207.

COMPOUNDS OF TUNGSTEN.

Tungsten and Oxygen.

488 Tungsten forms two definite oxides: tungsten dioxide WO_2, and tungsten trioxide WO_3. These combine together to form compounds analogous to the blue oxides of molybdenum (p. 861).

Tungsten Dioxide, WO_2.—This oxide is formed when a current of hydrogen is passed over the trioxide, WO_3, at a dull red-heat. It may also be obtained in the wet way by reducing the trioxide, mixed with hydrochloric acid, by means of metallic zinc, or by the action of water on the tetrachloride. In preparing it in the dry way care is needed, as if the temperature be too high metallic tungsten is formed, whereas if the heat be not sufficient, the intermediate blue oxide is produced. Tungsten dioxide is a brown powder of specific gravity, 12·1, which has a copper-red colour when crystalline trioxide is employed for its preparation. It is strongly pyrophoric, and must be cooled in hydrogen for some time before it is exposed to the air. It is slightly soluble in concentrated hydrochloric acid and sulphuric acid, yielding purple solutions. Oxidising agents convert it rapidly into the trioxide. It dissolves in potash with disengagement of hydrogen and the production of potassium tungstate :—

$$WO_2 + 2KOH = K_2WO_4 + H_2.$$

Tungsten Trioxide, WO_3.—This oxide occurs native as wolframine, a yellow powder found together with other tungsten minerals in Cumberland, near Limoges, in Connecticut, and in North Carolina. In order to prepare the trioxide, finely powdered wolfram is digested for a long time with hydrochloric acid, the mixture frequently shaken, the acid renewed, and a little nitric acid added towards the end of the process to oxidise the iron. This is continued until the acid has dissolved out the whole of the iron and manganese and the brown powder has become yellow coloured. The insoluble portion, consisting of tungsten trioxide and undecomposed wolfram and quartz, after being well washed, is shaken up with a solution of ammonia, which dissolves the liberated tungstic acid. The solution is

crystallised and the crystals are converted into the trioxide by ignition in the air. Wöhler converts the wolframite into calcium tungstate by fusing the finely powdered mineral for an hour with twice its weight of chloride of calcium and then lixiviating, when calcium tungstate remains behind. This is then decomposed by nitric acid, and tungsten trioxide is obtained by igniting the yellow precipitate thus thrown down. The native tungstate of calcium (scheelite) can also be decomposed in this way.

Tungsten trioxide is a bright canary-yellow coloured powder which becomes dark-orange on heating, but regains its bright yellow colour on cooling. A very slight admixture of sodium salt imparts to the oxide a greenish tint which no amount of oxidation can remove (Roscoe). It also becomes greenish on exposure to light. Tungsten trioxide has been obtained in the crystalline state by Debray, by igniting a mixture of tungstate and sodium carbonate in a current of hydrochloric acid, when the trioxide is obtained in olive-green rectangular prisms which sublime at a white heat. The crystalline trioxide has also been prepared by heating hydrated tungstic acid with borax in a porcelain tube (Nordenskjöld). The specific gravity of tungsten trioxide thus obtained is 6·34.

Tungstic Acid and the Tungstates.

489 Tungsten trioxide is an acid-forming oxide, and yields two tungstic acids, the normal acid, H_2WO_4, and metatungstic or tetratungstic acid, $H_2W_4O_{13}$, the salts of which correspond to the tetrachromates and tetramolybdates. In addition to the salts corresponding to these acids, a large number of other tungstates analogous to the polychromates and polymolybdates have been prepared, the formulæ of which are given in the following columns:

$M'_2WO_4 = M'_2O,WO_3$.	$M'_2W_8O_{25} = M'_2O,8WO_3$.
$M'_2W_2O_7 = M'_2O,2WO_3$.	$M'_4W_5O_{17} = 2M'_2O,5WO_3$.
$M'_2W_3O_{10} = M'_2O,3WO_3$.	$M'_6W_7O_{24} = 3M'_2O,7WO_3$.
$M'_2W_4O_{13} = M'_2O,4WO_3$.	$M'_8W_3O_{13} = 4M'_2O,3WO_3$.
$M'_2W_5O_{16} = M'_2O,5WO_3$.	$M'_{10}W_{12}O_{41} = 5M'_2O,12WO_3$.

Many of these crystallise with a varying number of molecules of water, forming well-developed crystals.

The tungstates also yield complex salts with many other acidic oxides analogous to the complex molybdates.

Tungstic Acid, H_2WO_4.—When a solution of a tungstate is precipitated by an acid in the cold, a white precipitate is thrown down consisting of hydrated tungstic acid, $H_2WO_4+H_2O$. This is soluble in water, possesses a bitter taste and reddens litmus. If, on the other hand, a solution of a tungstate be treated with an excess of hot acid, anhydrous tungstic acid, H_2WO_4, separates out as a yellow powder, and this is insoluble in water and in all acids except hydrofluoric acid. If pure tungsten hexachloride be exposed to the action of moist air, the red monoxychloride is first formed, and this soon passes into a fine flocculent mass of tungstic acid.

The tungstates are insoluble in water with the exception of those of the alkali-metals; and even of these, some tungstates of potassium and ammonium are only sparingly soluble. The tungstates of the alkaline-earth metals, and of the heavy metals are mostly amorphous powders, but they may be obtained in the crystalline state by double decomposition at a high temperature.

Metatungstic Acid, $H_2W_4O_{13}+7H_2O$.—The salts of this acid were discovered by Margueritte,[1] but the acid was first prepared by Scheibler.[2] For this purpose the barium salt is decomposed by dilute sulphuric acid or the lead salt with sulphuretted hydrogen. Metatungstic acid crystallises in small yellow octohedra which lose their water of crystallisation at 100°, and on ignition are converted into the trioxide. They are readily soluble in water and the solution possesses a harsh bitter taste. When the solution is concentrated by boiling, a white hydrate is deposited and afterwards the trioxide separates out. The metatungstates of the alkali metals are formed when the ordinary tungstates are boiled with tungstic acid until the filtrate gives no precipitate on addition of hydrochloric acid. The metatungstates of the other metals are, as a rule, easily soluble in water, and are best prepared by double decomposition of the barium salt with the corresponding sulphate or carbonate. The warm solutions usually yield the salts in amorphous masses when evaporated, but when concentrated over sulphuric acid they frequently crystallise. The metatungstates possess a bitter taste and do not yield a precipitate on addition of an

[1] *Ann. Chim. Phys.* 1846 [3], **17**, 475.
[2] *J. Pr. Chem.* 1861, **83**, 310.

acid, though on continued boiling ordinary tungstic acid is deposited.

Colloidal Tungstic Acid.—This modification of tungstic acid was discovered by Graham.[1] It is obtained by dialysing a 5 per cent. solution of tungstate of sodium to which a sufficient quantity of hydrochloric acid has been added to neutralise the soda. After several days, the liquid remaining on the dialyser is found to possess a bitter astringent taste and does not gelatinise on the addition of acids, even on boiling. On evaporating in a vacuum a colourless, vitreous, transparent gum-like mass is obtained, and this can be heated to 200° without losing its solubility, whilst at a red-heat it is transformed into tungsten trioxide, losing 2·4 per cent. of water. When moistened with water the colloidal acid becomes pasty and adhesive like gum, dissolving completely in one-quarter of its weight of water.

Sodium Tungstates.—The *normal salt*, $Na_2WO_4 + 2H_2O$, is prepared like the potassium salt, and is obtained on the large scale by fusing wolfram together with soda-ash. It crystallises in thin rhombic prisms which dissolve in four parts of cold and in two parts of boiling water.[2] The solution possesses a bitter taste and has an alkaline reaction. The crystals do not undergo alteration in the air and they are insoluble in alcohol. When heated to 200° it becomes opaque and loses its water, and at a red-heat fuses to a transparent liquid which crystallises on cooling.

Sodium Paratungstate, $Na_{10}W_{12}O_{41} + 28H_2O$.—This salt, which is the one known commercially as tungstate of soda, is prepared on the large scale by roasting wolfram with soda ash and lixiviating the fused mass. The boiling solution is nearly neutralised with hydrochloric acid and allowed to crystallise at the ordinary temperature, when it separates in large asymmetric crystals having the above composition. At a higher temperature crystals containing 25 and 21 molecules of water are formed. This salt is sometimes used in place of sodium stannate as a mordant in dyeing and calico printing, and is also employed for rendering cotton, linen, &c., uninflammable.[3]

Sodium Metatungstate, $Na_2W_4O_{13} + 10H_2O$, is formed by prolonged boiling of the normal salt with tungsten trioxide. It crystallises in octohedra probably belonging to the regular

[1] *Journ. Chem. Soc.* 1864, 325.

[2] Marignac, *Ann. Chim. Phys.* 1863 (3), **69**, 39.

[3] Versmann, *Reports of the Juries of the Exhibition of* 1862.

system. It is very efflorescent. Cold water dissolves 10·69 times its weight of this salt and boiling water dissolves it in all proportions. It loses its water at a red-heat (Marignac and Scheibler).

Potassium Tungstates.—The *normal salt*, K_2WO_4, is obtained by adding tungsten trioxide little by little to its own weight of fused potassium carbonate. On cooling a solution of the fused mass in hot water, or on allowing the solution to evaporate slowly at the ordinary temperature, normal potassium tungstate crystallises in large acicular anhydrous crystals or in large prismatic crystals, $K_2WO_4+2H_2O$ (Marignac). When the normal salt is boiled with a small quantity of water, or when tungsten trioxide is added to its boiling solution until no more dissolves, glistening scales of the *paratungstate*, $K_{10}W_{12}O_{41}+11H_2O$, are deposited. These dissolve more readily in hot than in cold water, and the solution has an acrid taste and acid reaction. When alcohol is added to the aqueous solution a precipitate is formed; this dissolves on warming but on cooling deposits scales of *potassium metatungstate*, $K_2W_4O_{13}+5H_2O$; a second hydrated salt containing eight molecules of water, crystallising in octohedra, is obtained from the mother-liquor of the normal tungstate.

Ammonium Tungstates.—The normal salt is not known. When a solution of tungstic acid in ammonia is allowed to evaporate over caustic lime, warty concretions of $(NH_4)_8W_3O_{13}+3H_2O$ are sometimes deposited, which easily give off ammonia. Needle-shaped crystals or tablets having the composition $(NH_4)_6W_7O_{24}+6H_2O$ are, however, usually deposited, whilst sometimes small asymmetric crystals of $(NH_4)_4W_5O_{17}+5H_2O$ likewise occur. If, however, the ammoniacal solution of the trioxide be allowed to evaporate whilst warm, monosymmetric crystals of $(NH_4)_{10}W_{12}O_{41}+5H_2O$ separate out. When tungsten trioxide is boiled with ammonia, quadratic prisms of *ammonium metatungstate* $(NH_4)_2W_4O_{13}+8H_2O$ are obtained. These are very soluble and effloresce quickly on exposure to the air. Besides these many other ammonium tungstates have been prepared (Marignac).

Normal Calcium Tungstate, $CaWO_4$.—This occurs native as scheelite in vitreous yellowish-white quadratic pyramids. Some of its chief localities are Zinnwald, Caldbeck Fell in Cumberland, Piedmont, Dalecarlia, in the Vosges, at Huntingdon in Connecticut, and at the Mammoth mining district in Nevada.

The crystals usually contain iron and are found in crystalline rocks in connection with tin-ore, topaz, apatite, wolfram, &c.

It is prepared artificially as a white insoluble precipitate by mixing solutions of calcium chloride and a normal tungstate, and can be obtained in the crystalline form of scheelite by heating the precipitate mixed with lime in a current of hydrochloric acid. If a hot solution of metatungstic acid be saturated with calcium carbonate, calcium metatungstate, $CaW_4O_{13}+10H_2O$, is obtained, crystallising in small quadratic octohedra.

Normal Barium Tungstate, $BaWO_4$, is obtained by fusing together the sodium salt with common salt and barium chloride, in the form of lustrous colourless crystals isomorphous with scheelite. *Barium Metatungstate*, $BaW_4O_{13}+9H_2O$, is obtained by mixing hot saturated solutions of the sodium salt and barium chloride with addition of some hydrochloric acid. It forms large quadratic pyramids which may be easily purified by recrystallisation from hydrochloric acid solution. If baryta water be added to the aqueous solution of the salt, needle-shaped crystals of $2BaWO_4+H_2O$ are deposited.

Lead Tungstate, $PbWO_4$, occurs as stolzite at Zinnwald in Bohemia, at Bleiberg in Carinthia, in Chili, and at Southampton, Massachusetts. It crystallises in red translucent quadratic pyramids having a specific gravity of 7·87 to 8·13.

Ferrous Tungstate, $FeWO_4$, occurs as the blue mineral farberite in Spain, closely resembling the commoner mineral wolfram, which contains manganese as an isomorphous constituent, $(Fe,Mn)WO_4$. This latter occurs in Cornwall, Cumberland, Ireland, France, the Erzgebirge, and various parts of the United States. Wolfram crystallises in the rhombic system in dark grey or brownish-black prisms having a metallic lustre and a specific gravity of 5 to 5·5.

Manganese Tungstate, $MnWO_4$, is found as hübnerite in Nevada in a vein from three to four feet wide.

Tungsten Tungstates.—By the partial reduction of tungsten trioxide a number of oxides of tungsten have been prepared, having a composition intermediate between that of the dioxide and trioxide. These have a blue or purple-red colour, and are combinations of the acidic trioxide with the more basic dioxide. Thus by the action of hydrogen on the trioxide at 250° the compound $W_3O_8=2WO_3,WO_2$ is formed, which has a deep blue colour; the same oxide, when prepared by heating ammonium

metatungstate to a red-heat, has a purple-red colour and metallic reflex.[1] Other blue oxides having the composition $W_2O_5 = WO_2,WO_3$; $W_4O_{11} = 3WO_3,WO_2$; $W_5O_{14} = 4WO_3,WO_2$ have been described; in addition Desi has obtained oxides containing less oxygen than the dioxide, by the action of concentrated sulphuric acid on metallic tungsten under suitable conditions.

Tungsten Bronzes.

490 These remarkable compounds, obtained by the partial reduction of the tungstates, are usually regarded as compounds of the tungstates with tungsten dioxide, but their exact constitution is as yet unknown. Owing to their bronze-like appearance and insolubility in acids and alkalis, they have been employed as bronze powder substitutes.

Tungsten sodium bronze was first obtained by Wöhler by the reduction of sodium tungstate with hydrogen, and may also be obtained by substituting coal-gas, zinc, iron or tin for hydrogen, or by means of electrolysis. It forms fine golden cubes, which have a specific gravity of 6·617, and conduct electricity well. On ignition in the air it oxidises and fuses. It is not attacked by any acid except hydrofluoric acid, nor is it acted upon by alkalis.[2] According to Philipp,[3] the products are a mixture of different compounds, the relative proportions of which vary according to the method of preparation, and the nature of the original tungstate. The substance obtained by heating the ditungstate in hydrogen, which was formerly supposed to have the composition $Na_2W_3O_9$, is, according to Philipp, $Na_5W_6O_{18}$, and has a golden-yellow colour. By the electrolysis of fused sodium paratungstate a blue bronze, $Na_2W_5O_{15}$, is obtained, which forms dark blue cubes or plates having a red reflex. A purple-red bronze, $Na_2W_3O_9$, is obtained by strongly heating a mixture of 12·9 grams of sodium carbonate and 68·9 grams of tungsten trioxide with 20 grams of tin foil, and a reddish-yellow bronze by fusing 60–80 grams of a mixture of two molecular proportions of sodium tungstate and one of the trioxide with 30 grams of tinfoil, for two hours. It forms reddish-yellow cubes and yields a brownish-yellow powder.

[1] Desi, *J. Amer. Chem. Soc.* 1897, **19**, 213.
[2] Knorre, *J. Pr. Chem.* 1883 [2], **27**, 63.
[3] Philipp, *Ber.* 1882, **15**, 499.

Tungsten Potassium Bronze is obtained in a similar manner to the sodium bronzes. It is obtained by adding tungsten trioxide to fused normal potassium tungstate until it no longer dissolves. The product is then gently heated in a stream of hydrogen and afterwards lixiviated with water, hydrochloric acid, and caustic potash, and lastly again with water. It forms small dark blue needles which possess a copper-red lustre. A compound crystallising in fine deep blue copper-lustrous quadratic prisms and pyramids, having the composition $K_2W_5O_{12} = K_2WO_4 + 4WO_2$, is obtained by passing a galvanic current through fused potassium polytungstate. This is not altered by the action of aqueous alkalis and acids.

Phosphotungstic Acids.—Tungstic acid combines with phosphoric and arsenic acids to form complex salts analogous to the corresponding molybdic acid derivatives. A very large number of these has been prepared, the relation $P_2O_5 : WO_3$ varying from 1 : 7 to 1 : 24. *Phosphoduodecitungstic acid*, $H_3PW_{12}O_{40} + xH_2O$, is obtained by evaporating a mixture of the requisite quantities of orthophosphoric acid and metatungstic acid or by the exact decomposition of the barium salt with sulphuric acid or the mercurous salt with hydrochloric acid. It crystallises in quadratic pyramids containing water of crystallisation, the amount of which is differently stated by different investigators. Two sodium salts are known, having the formulæ $Na_2HPW_{12}O_{40} + xH_2O$ and $Na_3PW_{12}O_{40} + xH_2O$, and are obtained by heating sodium hydrogen phosphate and tungstate solutions. In presence of an excess of hydrochloric acid the former salt is obtained in yellow crystals, whilst when the acid is gradually added with stirring until crystallisation commences the latter salt separates out in transparent colourless octohedra.

The number of complex phosphotungstates is very large, and many of them crystallise well.[1]

[1] See Scheibler, *Ber.* 1872, **5**, 801 ; Sprenger, *J. Pr. Chem.* 1880 (2), **22**, 48 ; Gibbs, *Amer. Chem. Journ.* 1880, **2**, 217, 281 ; 1882, **4**, 377 ; 1883, **5**, 361, 391 ; 1885, **7**, 31, 392 ; Kehrmann, *Ber.* 1887, **20**, 1805 ; 1811, 1891, **24**, 2326 ; 1892, **25**, 1966 ; *Annalen*, 1888, **245**, 45 ; *Zeit. anorg. Chem.* 1891, **1**, 428 ; Drechsel, *Ber.* 1887, **20**, 1452 ; Péchard, *Compt. Rend.* 1889, **109**, 301 ; 1890, **110**, 754.

Tungstosilicic Acids.

491 These peculiar compounds were discovered and investigated by Marignac,[1] who gives the following names and formulæ:

Silicodecitungstic acid, $4H_2O,SiO_2,10WO_3$.
Tungstosilicic acid, $4H_2O,SiO_2,12WO_3$.
Silicoduodecitungstic acid, $4H_2O,SiO_2,12WO_3$.

Silicodecitungstic Acid, $H_8W_{10}SiO_{36}+3H_2O$.—To prepare this acid gelatinous silica is boiled with ammonium polytungstate and the solution evaporated, ammonia being added from time to time. The ammonium salt, $(NH_4)_8SiW_{10}O_{36}+8H_2O$, is thus obtained in short rhombic prisms which are soluble in water; the solution is then precipitated by silver nitrate, the precipitate washed and decomposed by hydrochloric acid. On evaporating the filtrate in a vacuum the acid is left as a yellowish, glassy mass, and on exposure to air splits into fragments, which then deliquesce. Its salts have not been carefully examined.

On dissolving it in water and evaporating the solution, some silicic acid separates out, and the thick mother-liquor yields short asymmetric prisms of *tungstosilicic acid*, $H_8W_{12}SiO_{42}+20H_2O$, which are readily soluble in water and alcohol. It forms both normal and acid salts.

Normal Potassium Tungstosilicate, $K_8W_{12}SiO_{42}+20H_2O$, crystallises in ill-defined, rhombic prisms.

Acid Potassium Tungstosilicate, $H_4K_4W_{12}SiO_{42}+7H_2O$, occurs in two different forms, which crystallise from the same solution, and if one form be dissolved in water, the second form frequently crystallises out.

The *α*-compound forms transparent, thick, rhombic prisms; the *β*-compound crystallises in silky, soft, six-sided rhombic plates.

Silicoduodecitungstic or *Silicotungstic Acid*, $H_8SiW_{12}O_{42}+29H_2O$.—The salts of this acid are formed by boiling gelatinous silicic acid with the polytungstates of the alkali metals. To obtain the acid the salts are precipitated with mercurous nitrate and the washed precipitate decomposed by hydrochloric acid. It crystallises in large quadratic pyramids, which readily dissolve in water, alcohol, and ether. On gently heating it melts

[1] *Ann. Chim. Phys.* 1864 [4], **3**, 5.

in its water of crystallisation, and rhombohedra of $H_8SiW_{12}O_{42}+22H_2O$ are deposited. These are also formed by adding a little hydrochloric acid to the solution and concentrating.

It forms normal, acid, and double salts which, with the exception of the mercurous salt, are all soluble in water. Boiling hydrochloric acid converts the normal salts into acid salts without decomposing them further; alkalis decompose their solutions with the separation of silicic acid.

Normal Potassium Silicotungstate, $K_8SiW_{12}O_{42}+14H_2O$, forms hard granular crusts, consisting of prisms closely resembling cubes. It yields two acid salts; $H_4K_4SiW_{12}O_{42}+16H_2O$ forming transparent, glistening, hexagonal crystals, and $2H_5K_3SiW_{12}O_{42}+25H_2O$ crystallising in monosymmetric prisms.

Pertungstic Acid.—When a solution of sodium paratungstate is boiled for a few minutes with hydrogen dioxide, a yellowish solution is obtained, which no longer gives a precipitate with nitric acid. When the solution is allowed to evaporate in a vacuum, small white crystals having the formula $NaWO_4+H_2O$ are deposited, which are the sodium salt of the unknown pertungstic acid HWO_4. This salt is more soluble than sodium paratungstate, and when heated in a vacuum first gives off water, and finally decomposes with evolution of oxygen. Solutions of the salt liberate iodine from potassium iodide, and chlorine from hydrochloric acid.[1]

Tungsten and the Halogens.

492 *Tungsten and Fluorine.*—Tungsten trioxide dissolves in hydrofluoric acid, but on evaporation the oxide crystallises out unchanged. Neither a fluoride nor an oxyfluoride is known in the free state, but double salts of the latter with alkali fluorides have been obtained. The compound $2KF,WO_2F_2+H_2O$ is prepared by dissolving normal potassium tungstate in hydrofluoric acid, and adding potash till a permanent precipitate is just formed, and crystallises in scales which appear to be isomorphous with the corresponding molybdenum derivatives. The compound KF,WO_2F+H_2O is prepared by the action of a large excess of hydrofluoric acid on the polymolybdate, $K_{10}W_{12}O_{41}+11H_2O$, and forms rhombic crystals.[2]

[1] Péchard, *Compt. Rend.* 1891, **112**, 1060.

[2] Marignac, *Ann. Chim. Phys.* 1863 (3), **69**, 70.

493 Four compounds of tungsten and chlorine are known, viz.:

(1) Tungsten dichloride . . . WCl_2.
(2) Tungsten tetrachloride . . WCl_4.
(3) Tungsten pentachloride . . WCl_5.
(4) Tungsten hexachloride . . WCl_6.

Tungsten Dichloride, WCl_2.—This body may be obtained in pale grey crusts by reducing the hexachloride at a moderately high temperature in hydrogen. It is, however, best prepared by heating the tetrachloride in a current of carbon dioxide. For this purpose the temperature of a moderately hot zinc bath is used. The dichloride is a non-volatile loose grey powder without lustre or crystalline structure. It alters perceptibly on short exposure to the air and dissolves slightly in water forming a brown solution. The remainder is converted into the brown oxide, a slow evolution of hydrogen occurring (Roscoe).

Tungsten Tetrachloride, WCl_4, is produced by the incomplete reduction of the hexachloride or pentachloride by hydrogen, and forms the non-volatile residue obtained by the distillation of the hexachloride in hydrogen. In order to obtain it in the pure state a mixture of hexa- and pentachloride is distilled at a low temperature from a bath of sulphuric acid in a current of dry hydrogen or carbon dioxide and the volatile pentachloride poured back again once or twice over the residue to convert into the tetrachloride the lower chlorides or metal which are also formed. Tungsten tetrachloride is a loose soft crystalline powder of a greyish-brown colour. It is highly hygroscopic, though not so much so as the pentachloride. It is partially decomposed by cold water into the brown oxide and hydrochloric acid. The tetrachloride is non-volatile and infusible under ordinary pressure, but on heating it decomposes into pentachloride, which distils off, and dichloride, which remains behind. On heating in hydrogen to a temperature above the melting-point of zinc the tetrachloride is reduced to metallic tungsten, some of which is deposited as a black tinder-like powder and undergoes spontaneous ignition on exposure to air (Roscoe).

Tungsten Pentachloride, WCl_5.—This compound is formed by the incomplete reduction of the hexachloride in a current of hydrogen. If the temperature be kept but slightly above the boiling-point of the hexachloride the dark red colour of its vapour is seen to disappear and a light greenish-coloured vapour

takes its place, and this soon condenses either to black drops or to long shining black needle-shaped crystals. After two or three distillations in hydrogen a pure volatile product is obtained. For the production of the pentachloride it is, however, more convenient to reduce the hexachloride at a higher temperature, when a further loss of chlorine takes place, the solid non-volatile tetrachloride remaining behind and the volatile pentachloride distilling over. The latter compound only requires redistillation in order to obtain it in the pure state. Tungsten pentachloride crystallises in long black shining crystals, but if quickly condensed the crystalline powder possesses a dark green colour resembling potassium manganate. It melts at 248°, boils at 275·6°, and is extremely hygroscopic, the crystals becoming instantly covered with a dark golden-green film on exposure to air, whilst the small particles are converted into liquid. The crystals do not decrepitate on cooling like those of the hexachloride. On treatment with large quantities of water, the pentachloride forms an olive-green solution, although the greater part is at once decomposed into the blue oxide and hydrochloric acid. The vapour density of tungsten pentachloride taken in sulphur vapour at 440° was found to be 186·5 (H = 1), whilst in mercury vapour at 350° it was found to be 177·8 (Roscoe). The formula WCl_5 requires a vapour density of 179·3.

Tungsten Hexachloride, WCl_6.—This substance is prepared by heating metallic tungsten in an excess of dry and pure chlorine. It is necessary for the preparation of the pure compound that every trace of oxygen and of moisture be excluded, as otherwise some red oxychloride is invariably formed, and this cannot easily be separated from the hexachloride by distillation. Metallic tungsten takes fire at a moderate heat in dry chlorine, and the action goes on by itself until all the chlorine has disappeared.

In order to obtain the hexachloride in quantity the metal is first ignited in a current of dry hydrogen; then the hydrogen is completely displaced by a current of dry carbon dioxide and lastly chlorine free from air substituted, and the tube or retort moderately heated. At the commencement of the operation a slight sublimate of red needle-shaped crystals of the oxychloride is frequently formed owing to the unavoidable presence of traces of oxygen, but this is easily driven to the end of the tube beyond the point at which it is intended to collect the hexachloride. On raising the temperature of the metal, a

granular sublimate of dark violet opaque crystals of the hexachloride makes its appearance, and if in large quantity the hexachloride collects as a blackish-red liquid. In order to saturate this liquid, it is slowly distilled in a current of chlorine. The dark violet crystals decrepitate on cooling; and the crystalline mass thus readily breaks up into a powder.

When pure, the solid hexachloride does not undergo any change even in moist air, but in the presence of the slightest trace of oxychloride it at once absorbs moisture, evolving copious fumes of hydrochloric acid and changing in colour from violet to brown. Water does not act upon the pure hexachloride, but on boiling decomposition occurs. If, however, the oxychloride be present the whole is suddenly decomposed by cold water into a greenish oxide. It is soluble in carbon bisulphide, crystallising from the solution in six-sided plates.

The melting-point of the hexachloride is 275°; it boils under a pressure of 759·5 mm. at 346°·7. The vapour density of tungsten hexachloride has been determined in sulphur vapour and in mercury vapour; at 440°, the mean experimental density is 168·8, whilst at 350° the density is 190·9, the calculated density being 196·9. The alteration of the density from 191 at 350°, only 3° above the boiling-point, to 169 at 440° points to the fact that dissociation occurs. That this is the case is shown by the fact that when a current of dry carbon dioxide is passed through the fused hexachloride a continuous liberation of the chlorine takes place, whereas the pentachloride treated in the same way does not undergo a similar decomposition.

Tungsten Oxychlorides.—The *monoxychloride* $WOCl_4$, and the *dioxychloride* WO_2Cl_2, have been studied by Blomstrand and Riche. The dioxychloride is best obtained by passing chlorine over the brown oxide. Combination takes place at a moderate temperature, the oxide becoming covered with a whitish crust which on increase of temperature sublimes without melting, condensing in small square scales of a light lemon-yellow colour. The dioxychloride volatilises at a temperature approaching redness with partial decomposition; the crystals do not fuse and are not acted upon by moist air or cold water. Even when boiled with water the dioxychloride is not completely decomposed.

The splendid red needle-shaped crystals of the monoxychloride, first prepared by Wöhler, are obtained by passing the vapour of the hexachloride over heated oxide or dioxychloride,

$$WO_3 + 2WCl_6 = 3WOCl_4$$

and also by acting on the trioxide with phosphorus pentachloride.[1] The crystals melt at 210°·4, and the liquid boils at 227°·5, forming a red vapour rather lighter coloured than that of the hexachloride. On repeated distillation over red-hot charcoal in a current of chlorine the hexachloride is formed. On exposure to the air the monoxychloride becomes at once covered with a yellowish crust of tungstic acid. The vapour density at 350° is found to be 171·5 and at 440° 173, the theoretical density being 169·7 (Roscoe).

494 Bromine acts rapidly on red-hot tungsten, forming dark bromine-like vapours, which condense to a crystalline sublimate. Special precautions similar to those taken in the preparation of the chlorides must also be employed for the bromides, as the oxybromides formed in the presence of air and moisture possess almost the same colour as the bromide, and therefore the detection of the impurity is not so easy as is the case with the chloride.

Tungsten Dibromide, WBr_2, is formed by the reduction in hydrogen of the pentabromide, heated in a bath of fused zinc chloride. A residue of non-volatile dibromide remains in the form of a bluish-black velvety crystalline powder.

Tungsten Pentabromide, WBr_5.—By the action of an excess of bromine on tungsten a penta- and not a hexabromide is obtained. Indeed the pentabromide itself evolves bromine on standing. The pentabromide forms dark crystals having a metallic lustre resembling iodine, melting at 276°, and boiling at 333°. It is at once decomposed by an excess of water into hydrobromic acid and the blue oxide. When the pentabromide is heated in a current of hydrogen, the metal is formed in the state of pyrophoric powder.

Tungsten Oxybromides, corresponding to the oxychlorides, exist. The *dioxybromide* WO_2Br_2, is formed by passing bromine vapour over red-hot tungsten dioxide. It forms light-red transparent crystals which yield a yellow powder. They do not melt, but volatilise at a temperature approaching a red-heat, and they are not acted upon by water. The *monoxybromide* $WOBr_4$ is formed under the same circumstances as the last-named compound as brownish-black shining needles, which are readily fusible and can be separated from the dioxybromide by gently heating, when the latter compound remains behind. It melts at 277°, boils at 327°·5, and is decomposed by contact with water.

[1] Schiff, *Annalen*, 1879, **197**, 185.

Tungsten Di-iodide, WI_2, is obtained in the form of green metallic scales, when iodine vapour is passed over the metal heated to redness (Roscoe).

Tungsten and Sulphur.

495 *Tungsten Disulphide*, WS_2, is obtained by the action of sulphur, sulphuretted hydrogen, or carbon bisulphide on ignited metallic tungsten. It is also prepared by heating tungsten trioxide in a crucible with six times its weight of cinnabar. It forms soft, black, needle-shaped crystals, which soil the fingers like graphite.

Tungsten Trisulphide, WS_3, is obtained only in the wet way by dissolving tungsten trioxide in sulphide of ammonium and precipitating with an acid, or by saturating an aqueous solution of an alkali tungstate with sulphuretted hydrogen, and acidifying. When dry it is black, yielding a liver-coloured powder. It dissolves slowly in cold water, and is precipitated by sal-ammoniac and acids. It is easily dissolved by potassium carbonate, and also by ammonia. It is reduced when heated with cyanide of potassium to the disulphide, this latter compound being unaltered by fusion with excess of the reagent.

The Sulphotungstates.—The sulphotungstates of the alkali and alkaline earth metals are prepared by dissolving the trisulphide in the corresponding hydrosulphide, or by treating the corresponding tungstate with sulphuretted hydrogen. The ammonium salt $(NH_4)_2WS_4$, is deposited from concentrated solution in yellowish-red crystals; the potassium salt, K_2WS_4 forms anhydrous yellow crystals, whilst the sodium salt, Na_2WS_4 crystallises with difficulty.

Tungsten and Nitrogen and Phosphorus.

496 Tungsten does not directly combine with nitrogen, and neither the metal nor the dioxide is attacked when strongly heated in ammonia. By the action of ammonia on the oxytetrachloride or the hexachloride in the cold, a black semi-metallic powder is obtained, which has the composition, W_2N_3. It is insoluble in caustic soda, nitric acid, and dilute sulphuric

acid, but is converted by concentrated sulphuric acid into ammonia and tungstic acid.[1]

By the action of ammonia on tungsten trioxide at a dull red heat Wöhler obtained a black amorphous product, the formula of which, deduced from his analysis, and using the modern atomic weight of tungsten, is $W_4N_5H_2O_2$, whilst Rideal finds the formula, $W_5N_6H_3O_5$. It is insoluble in acids and alkalis, but dissolves in sodium hypochlorite, and on ignition decomposes, ammonia, nitrogen, and hydrogen being evolved. Wöhler gave to it the name *tungsten nitretamidoxide.*

Phosphides of Tungsten.—Phosphorus and tungsten combine directly when the finely powdered metal is heated to redness in phosphorus vapour, a dark green powder, of the composition W_3P_4, being formed. Another compound, W_2P, is obtained when a mixture of phosphorus pentoxide and tungsten trioxide, in the proportion of two molecules of the former to one molecule of the latter, is reduced at a high temperature in a charcoal crucible,[2] and forms a vesicular mass, the hollow portions of which contain large crystals.

Detection and Estimation of Tungsten.

497 All the insoluble tungsten compounds can be converted into soluble tungstates by fusion, either with a caustic alkali alone, or with the addition of nitre. The solution when brought into contact with zinc and hydrochloric acid becomes blue-coloured, owing to the formation of the blue tungsten oxides (or tungsten tungstates), and when ammonium sulphide is added to the colourless solution, and then dilute hydrochloric acid, a brown precipitate of tungsten sulphide is obtained, whereas hydrochloric acid alone precipitates tungstic acid, which on heating turns yellow. If the tungsten compounds are fused with a small quantity of tin in the reduction flame with microcosmic salt, a blue bead is obtained, whilst tungsten compounds containing iron yield in the reduction flame a blood-red bead.

Tungsten is determined *quantitatively* as the trioxide. For the purpose of determining the quantity contained in wolfram, for instance, the finely powdered mineral is heated with aqua regia, evaporated to dryness, the residue treated with water,

[1] Wöhler, *Annalen*, 1850, **73**, 190; 1858, **105**, 258; Rideal, *Journ. Chem. Soc.* 1889, i. 41.

[2] Wöhler, *Journ. Chem. Soc.* 1853, 94.

the soluble chlorides of iron and manganese filtered off, and the insoluble tungstic acid washed with alcohol and dissolved in ammonia. The solution is then evaporated down, and the residue heated gently, and afterwards ignited in presence of air, when the trioxide remains, and is weighed.

Atomic Weight of Tungsten.—The atomic weight of tungsten has been determined by numerous investigators. Schneider[1] by the reduction of tungsten trioxide to metal and oxidation of the metal to trioxide found the average value 182·60, whilst Marchand[2] found the slightly higher number 182·88. Roscoe[3] by the same method obtained the number 182·41, and by the analysis of the hexachloride the number 182·67, whilst Waddell[4] by the reduction of the trioxide found the higher number 183·12. More recently Pennington and Smith and Desi,[5] have found the still higher number 183·42 by Schneider's method, but their results have been criticised by Schneider[6] as untrustworthy, and the most probable value appears to be 182·7 (O = 15·88).

URANIUM. U = 237·8.

498 The mineral known as pitchblende was formerly believed by certain chemists to be an ore of either zinc or iron, whilst by others it was thought to contain tungsten. Klaproth, in 1789, was the first to point out the existence in this mineral of a peculiar metal, to which he gave the name of uranium, in remembrance of Herschel's discovery of the planet Uranus, in the year 1781. The body obtained by Klaproth by the reduction of the calx of uranium was supposed by all the chemists who subsequently investigated the subject to be the metal, until Péligot[7] in 1842 proved this body to be an oxide. Péligot likewise isolated the metal and determined its equivalent.

Uranium is not a very abundant element, and its chief ore is pitchblende. This consists of impure uranoso-uranic oxide, U_3O_8, and is found in Cornwall, at Joachimsthal, Johanngeorgenstadt, Adrianople, and other localities. Uranium is also found as phosphate in uranite or uranium-mica, as carbonate in liebigite, whilst as urano-tantalite or samarskite it is found combined with

[1] *J. pr. Chem.* 1850, **50**, 152. [2] *Annalen*, 1851, **77**, 261.
[3] *Mem. Manch. Lit. and Phil. Soc.* (3), **5**, 77; *Annalen*, 1872, **162**, 366.
[4] *Amer. Chem. Journ.* 1886, **8**, 280.
[5] *Zeit. anorg. Chem.* 1895, **8**, 198, 205. [6] *J. pr. Chem.* 1896 (2), **53**, 288.
[7] *Ann. Chim. Phys.* 1842 [3], **5**, 5.

niobium and tantalum. Pitchblende is the best source of uranium, this mineral usually containing from 40 to 90 per cent. of uranoso-uranic oxide, U_3O_8. The following analysis by Ebelmen gives the composition of an average specimen of pitchblende:

Uranoso-uranic oxide, U_3O_8	75·23
Lead sulphide	4·82
Silica	3·48
Lime	5·24
Magnesia	2·07
Soda	2·05
Ferrous oxide	3·10
Manganous oxide	0·82
Carbon dioxide	3·32
Water	1·85
	101·98

The uranium minerals appear almost always to contain the element helium.

The process recommended by Wöhler for the extraction of uranium from pitchblende is as follows: The powdered mineral is digested with sulphuric acid, small quantities of nitric acid being added from time to time to the mixture. As soon as the precipitate is transformed into a white powder and partially dissolved, the excess of sulphuric acid is driven off, and the residue digested with water. This leaves a residue of silica, lead sulphate, and the basic sulphates and arsenates of bismuth. The filtered liquid is then warmed, and a current of hydrogen sulphide passed through it, when arsenic, antimony, copper, and the rest of the lead and bismuth are thrown down. The filtrate is then oxidised by nitric acid, and an excess of ammonia added; the precipitate containing the ferric and uranic hydroxides is next washed with ammonia, and then digested at 100° with a concentrated solution of ammonium carbonate containing an excess of ammonia. The uranic hydroxide dissolves, and the yellow double carbonate of uranium and ammonium crystallises out on cooling. The mother-liquor still contains a small quantity of uranium, together with cobalt, nickel, and zinc, and these latter metals are precipitated by sulphide of ammonium, which is added drop by drop until no further brown precipitate falls. The filtered liquid is boiled,

and this soon deposits a yellow precipitate of ammonium uranate. Another process described by Péligot depends upon the facility with which uranyl nitrate crystallises, and upon its ready solubility in ether. Finely powdered pitchblende is treated with nitric acid, the acid solution evaporated to dryness, and the residue washed with water, leaving a residue consisting of lead sulphate and ferric arsenates. The filtered liquid has a greenish-yellow colour, and yields on concentration a radiated crystalline mass. This is then dried, the mother-liquor evaporated, and the whole again crystallised. Long prismatic crystals are thus deposited, which must be washed with a small quantity of cold water, the washings being again used for dissolving another portion of the crude nitrate. After having been dried, the crystals are shaken up with ether, when uranyl nitrate dissolves, and is obtained in the form of crystalline needles on evaporation of the ethereal solution.

Metallic Uranium was first prepared in the pure state by Péligot, who obtained it by the action of sodium or potassium on uranium tetrachloride, a mixture of the tetrachloride, potassium chloride and sodium being usually employed.[1] It is however, best obtained by heating 500 parts of the oxide, U_3O_8, with 40 parts of sugar charcoal in a carbon tube, closed at one end, in the electric furnace. The product contains a little carbon, which is partially removed by heating it in a crucible brasqued with uranium oxide, and enclosed in a larger crucible brasqued with titanium to protect the uranium from the action of nitrogen.[2]

Pure uranium has a white colour, and takes a high polish ; it has a specific gravity of 18·7 at 14°, a specific heat of 0·02765, and in the powdered state oxidises on exposure to the air and decomposes water slowly at the ordinary temperature, and more quickly at the boiling point. In the same condition it burns in oxygen at 170°, in fluorine at the ordinary temperature, in chlorine at 180°, in bromine at 210°, in iodine at about 260°, and in sulphur vapour at 500°. It melts at a high temperature, and volatilises more readily than iron, condensing in small, non-magnetic spheres, free from carbon.[3] It readily combines with nitrogen at 1000°.

[1] *Ann. Chim. Phys.* 1869 (4), **17**, 368.

[2] Moissan, *Compt. Rend.* 1896, **122**, 1088.

[3] Zimmermann, *Annalen*, 1883, **216**, 1 ; Moissan, *Compt. Rend.* 1893, **116**, 1429 ; 1896, **122**, 1088.

Both metallic uranium and many of its compounds emit the so-called Becquerel's rays, which in many of their properties resemble the x-rays of Röntgen.

COMPOUNDS OF URANIUM.

Uranium and Oxygen.

499 Uranium combines with oxygen to form two well-defined oxides, UO_2 and UO_3, and these combine, forming intermediate oxides. The dioxide is a basic oxide, and gives rise to the uranous salts, in which the metal is tetravalent. The trioxide, like the corresponding oxide of the other metals of this group, behaves as an acid-forming oxide, yielding salts known as the *uranates*, analogous to the chromates, molybdates and tungstates. As with the other trioxides of the group uranium trioxide also yields a large number of derivatives in which only one of the three oxygen atoms is replaced by negative groups; these may be regarded as derivatives of the compound radical *uranyl* UO_2. This radical has more decidedly basic properties than the corresponding radicals derived from the other metals, and the derivatives, therefore, correspond to the salts of basic oxides, whilst the similar compounds of the other metals are more nearly allied to the acid chlorides, such as sulphuryl chloride, SO_2Cl_2, and phosphoryl chloride, $POCl_3$. As already mentioned it was long supposed that the dioxide was the free metal, and what is now known as the trioxide was regarded as a compound of the metal with one atom of oxygen.

Uranium Dioxide, UO_2.—This oxide, formerly mistaken for the metal uranium, is obtained by heating the uranoso-uranic oxide or uranic oxalate in a current of hydrogen. Thus prepared it is a pyrophoric powder, having a brown or copper-red colour, and a specific gravity of 10·15. When heated in the air it takes fire, and is completely converted into the oxide, U_3O_8. It dissolves in strong acids, forming the green uranous salts. It may be obtained in jet black octohedra isomorphous with thoria by fusing with borax, and then removing the latter with dilute hydrochloric acid.[1]

Uranous Hydroxide is precipitated in reddish-brown flakes,

[1] Hillebrand, *Zeit. anorg. Chem.* 1893, **3**, 249.

which become black on ebullition, by adding an alkali to a uranous solution. It dissolves easily in dilute acids, whilst the calcined oxide is only difficultly soluble in these liquids.

Uranic Oxide, UO_3, or *Uranyl Oxide* $(UO_2)O$.—When uranyl nitrate, obtained by dissolving the lower oxides in nitric acid, is heated in a glass tube to 250° so long as acid fumes escape, this oxide is left behind in the form of a brownish-yellow powder.

Uranic Hydrate, UO_3+2H_2O, cannot be obtained by precipitating a uranic salt by an alkali, the precipitate thus formed consisting of an alkali uranate. It may, however, be prepared, according to Berzelius, by gently calcining the nitrate in a sand-bath as long as nitric acid is evolved. The residue contains uranic hydrate mixed with a basic salt, which can be removed by washing with boiling water. It may likewise be obtained by evaporating a solution of uranyl nitrate in absolute alcohol, at a moderate heat, until a yellow mass remains, consisting of the hydroxide, $UO_2(OH)_2+H_2O$. This hydrate loses half its water at 100°, or in a vacuum at the ordinary temperature, but at a temperature of 400° it begins to lose oxygen, and is converted into uranoso-uranic oxide. Uranic hydroxide is yellow, and has a specific gravity of 5·92. It does not undergo change in the air, nor does it absorb carbonic acid.

This oxide, as mentioned above, yields by the action of acids the *uranyl* salts, whilst with bases it gives rise to the *uranates*. The former have a yellow colour, and most of them possess a remarkable fluorescence, which they impart to glass. The absorption bands exhibited by these compounds have been studied by Becquerel and others. These salts are highly sensitive to light and have been employed for photographic purposes. The most important are described in the sequel, together with the other uranium salts.

The Uranates.—The alkali uranates are obtained by precipitating a uranic salt with an alkali, those of the alkaline earths and other metals by precipitating a mixture of a uranic salt and a corresponding metallic salt with ammonia. They are also formed when a mixture of metallic uranate and the acetate or carbonate of the metal is heated in the air. The uranates generally have the composition $M_2O.2UO_3$, and correspond to the dichromates. They are yellow, insoluble in water but soluble in acids, and are decomposed by heat, like uranic oxide itself.

Potassium Di-uranate, $K_2U_2O_7$. This is obtained as a pale

orange-yellow coloured powder by precipitating a uranic salt with an excess of potash, or by fusing uranyl chloride with potassium chloride and sal-ammoniac.

Sodium Di-uranate, $Na_2U_2O_7$, is obtained like the potassium salt, and is known as *uranium yellow*, being used for painting on glass and porcelain, as well as for preparing the yellow glass known as uranium glass. It is prepared on a large scale by roasting 100 parts of pitchblende, containing 45 per cent. of U_3O_8, with 14 parts of lime in a reverberatory furnace. The resulting calcium uranate is treated with dilute sulphuric acid, and the solution of uranic sulphate thus obtained is mixed with sodium carbonate. The uranium is precipitated, together with the other metals, but re-dissolves in an excess of the alkali. On treating this liquid with dilute sulphuric acid, a hydrated sodium uranate, or uranium yellow, $Na_2U_2O_7+6H_2O$, is obtained.[1]

Ammonium Uranate. This salt sometimes occurs in commerce as a fine deep yellow-coloured precipitate, termed, like the sodium salt, uranium yellow. It is easily obtained by adding ammonium chloride or sulphate to a boiling solution of sodium uranate, washing the resulting precipitate, and drying at a gentle heat. When heated to redness this salt yields pure uranoso-uranic oxide, and serves therefore as the raw material for the preparation of other uranium compounds.

Green Oxide of Uranium, $U_3O_8=UO_2+2UO_3$, occurs more or less pure in pitchblende. The pure oxide can be obtained by gently heating the trioxide or the dioxide in the air in the form of a satiny dark-green powder, having a specific gravity of 7·2, and soluble in strong acids.

Black Oxide of Uranium or *Uranium Pentoxide*, $U_2O_5=UO_2+UO_3$, is formed when the other oxides, or ammonium uranate, are strongly ignited in the air. Zimmermann states that it possesses no constant composition.[2]

500 *Uranium Tetroxide*, UO_4. When a very dilute solution of hydrogen dioxide is added to one of uranyl nitrate, a yellowish-white precipitate of UO_4+2H_2O is formed, which evolves chlorine when treated with hydrochloric acid.[3]

Sodium Peruranate, $Na_4UO_8+8H_2O$, is formed in a similar manner to the preceding compound, and crystallises in golden-yellow needle-shaped crystals, which are somewhat more stable than the potassium salt. If the minimum quantity of caustic

[1] Patera, *J. pr. Chem.* 1854, **61**, 397.
[2] *Annalen*, 1885, **232**, 276.
[3] Fairley, *Journ. Chem. Soc.* 1877, i. 127.

soda be employed, a red crystalline salt separates out, having the composition $NaUO_5+3H_2O$, or $Na_2U_2O_{10}+6H_2O$. This may be regarded as uranyl sodium peruranate $(UO_2)Na_2UO_8+6H_2O$, and, in the same way, the tetroxide may be considered to be uranyl peruranate $(UO_2)_2UO_8$.

Potassium Peruranate, $K_4UO_8+10H_2O$, is a yellow or orange precipitate formed when alcohol is added to a solution of uranyl nitrate, caustic potash, and hydrogen dioxide. The salt is very unstable, losing oxygen, and rapidly absorbing carbon dioxide on exposure.

Uranium and the Halogens.

501 *Uranium Tetrafluoride* or *Uranous Fluoride*, UF_4, is obtained in the form of a voluminous green powder, when hydrofluoric acid is added to a solution of uranous chloride. It is insoluble in water and hydrofluoric acid, and when heated in the air it leaves a green residue of oxide. When ignited in hydrogen it loses hydrofluoric acid, leaving a reddish-brown residue.[1]

Uranous fluoride forms double salts with the alkali fluorides. Potassium urano-fluoride, $KF.UF_4$, is obtained by the action of reducing agents, such as formic and oxalic acids, under the influence of light, upon potassium urano-oxyfluoride, described below. It is a green powder, resembling uranous fluoride, insoluble in water and in dilute acids.

Uranyl Fluoride, UO_2F_2 was obtained by Smithells[2] in two modifications. The *a*-compound is obtained by carefully heating the tetrafluoride in presence of air as a white crystalline sublimate, which is very hygroscopic and yields a yellow solution; the *β*-derivative is formed by evaporating a solution of the oxide, U_3O_8, in hydrofluoric acid, when it remains as yellow mass. Both combine with potassium fluoride, yielding *Potassium Uranium Oxyfluoride*, $UO_2F_2 3KF$, which is a lemon-yellow crystalline precipitate, and is also formed when an excess of potassium fluoride is added to a solution of uranyl acetate. It is trimorphous (Baker).[3] Corresponding sodium, ammonium, and barium salts are known (Bolton).

Uranium Trichloride, UCl_3, is obtained by heating the tetra-

[1] Carrington Bolton, *Berlin Acad. Ber.* 1866, 299.
[2] *Journ. Chem. Soc.* 1883, i. 125.
[3] *Journ. Chem. Soc.* 1879, i. 763.

chloride in hydrogen,[1] or by the continued reduction of uranyl salts with zinc and hydrochloric acid.[2] It is a reddish-brown powder, and dissolves readily in water, forming a red solution, which gradually becomes green with evolution of hydrogen.

Uranium Tetrachloride, or *Uranous Chloride*, UCl_4. This is produced with vivid incandescence, when chlorine is passed over metallic uranium, and is also formed by igniting uranium dioxide in hydrogen chloride. It is best prepared by passing chlorine over a heated mixture of charcoal and any of the uranium oxides. Some pentachloride is simultaneously formed, and may be removed by heating the product in a current of carbon dioxide. It crystallises in splendid dark-green octohedra, having a metallic lustre, and volatilising at a red heat to form red vapours having the normal specific gravity of 13·3. It is extremely deliquescent, fumes strongly on exposure to the air, and dissolves readily in water, with evolution of heat and formation of a deep, emerald-green solution. This, when concentrated in a vacuum, leaves an amorphous deliquescent mass of uranous chloride, but when evaporated by heat it decomposes, yielding a soluble residue, probably consisting of the oxychloride. Solutions of uranous chloride yield with alkalis a precipitate of *uranous hydrate*. The solution acts as a powerful deoxidising agent, reducing gold and silver salts, and converting ferric chloride into ferrous chloride. It was by the analysis of this chloride that Péligot ascertained that the supposed metal was in reality an oxide.

Uranium tetrachloride combines directly with ammonia, forming the compound $3UCl_4 + 4NH_3$.

Uranium Pentachloride, UCl_5, is obtained by the direct union of the tetrachloride with chlorine. It exists in two distinct forms, according as it is produced slowly or quickly. When the current of chlorine is slow the pentachloride of uranium forms long dark needle-shaped crystals, which reflect light with a green metallic lustre, but are of a splendid ruby-red colour when viewed by transmitted light. If the rate at which the chlorine passes be rapid, the pentachloride is deposited in the form of a light brown mobile powder. The magnificent octohedral crystals of the tetrachloride are always deposited in quantity in that part of the tube nearest the heated mixture, then the black needle-shaped crystals of the pentachloride are

[1] Péligot, *Ann. Chim. Phys.* 1842, **5**, 20.
[2] Zimmermann, *Annalen*, 1882, **213**, 320.

formed, mixed with more or less of the brown powder, which is generally carried a considerable distance along the tube. Both the black crystals and the brown powder are extremely hygroscopic, yielding yellowish-green liquids on exposure to the air for a few minutes, and hissing and giving off fumes of hydrochloric acid when thrown into water. Uranium pentachloride cannot be volatilised without partial decomposition, as when heated, either alone or in an atmosphere of chlorine, or carbon dioxide, uranium tetrachloride and free chlorine are formed. This dissociation begins in an atmosphere of carbon dioxide at 120°, and is complete at 235°, when the percentage of chlorine contained in the residue shows that one-fifth of the chlorine has been driven off. The tetrachloride when similarly heated loses no chlorine.[1]

Uranyl Chloride or *Uranium Oxychloride*, UO_2Cl_2, is formed when dry chlorine gas is passed over uranium dioxide at a red heat. The tube then becomes filled with the orange-yellow vapour of this compound, which solidifies to a yellow crystalline mass, and is easily fusible, but not very volatile.

Uranyl chloride is soluble in water, alcohol, and ether, and its aqueous solution yields on evaporation crystals of the hydrate, $UO_2Cl_2 + H_2O$. This may be obtained in solution by acting upon uranic oxide with hydrochloric acid, or by oxidising a solution of uranous chloride with nitric acid.

Uranyl chloride forms double chlorides with the chlorides of the alkali metals. The ammonium salt, $2NH_4Cl + UO_2Cl_2 + 2H_2O$, crystallises in rhombohedra from a syrupy solution of the mixed salts. The potassium salt, $2KCl + UO_2Cl_2 + 2H_2O$, is obtained by dissolving potassium uranate in excess of hydrochloric acid, adding chloride of potassium, and evaporating, when large rhombic tables separate out, which have a yellowish-green colour, and are very soluble. Uranyl chloride also combines with the hydrochlorides of the organic bases (Greville Williams).

Uranium tetrabromide, UBr_4, is obtained by heating in an atmosphere of bromine vapour a previously ignited mixture of uranous oxide and six times its weight of starch. The bromide is deposited in the more strongly-heated portions of the tube in brown tablets. The specific gravity of its vapour is 19·5. It fumes in the air, and is very deliquescent.

Uranyl Bromide or *Uranium Oxybromide*, UO_2Br_2, is obtained

[1] Roscoe, *Journ. Chem. Soc.* 1874, 933.

by treating uranous oxide with bromine and water, or by dissolving uranic oxide in hydrobromic acid. On evaporation yellow needles are deposited, which have a styptic taste.

Uranium Tetriodide, UI_4, described by Rammelsberg, is the only known compound of uranium and iodine. It is obtained by dissolving uranous hydroxide in hydriodic acid. A green solution is thus obtained, which decomposes on evaporation.

Uranium and Sulphur.

502 *Uranium Sesqui-Sulphide*, U_2S_3, is prepared by heating UBr_3 in sulphuretted hydrogen and yields uranium monosulphide US when heated in hydrogen.[1]

Uranous Sulphide, US_2, is obtained, according to Péligot, when metallic uranium is heated in sulphur vapour. The mass takes fire and an amorphous greyish-black powder is obtained which becomes crystalline when ignited in absence of air. It may also be formed by the action of sulphuretted hydrogen on uranium tetrachloride heated to redness. Sulphide of ammonium also gives a black precipitate of the hydrated sulphide with uranium salts. When exposed to moist air the sulphide gives off hydrogen sulphide and is converted into uranyl sulphide, UO_2S.

Uranyl Sulphide, UO_2S, is precipitated when sulphide of ammonium is added to a solution of uranic nitrate. It oxidises quickly on exposure to air, dissolves easily in acids and also in ammonium carbonate. When heated until all the ammonium sulphide has been driven off, it decomposes into sulphur and the dioxide. If air be excluded the ammonium sulphide acts as a reducing agent and the residual black powder has the composition U_7O_{10}. When exposed to air, or if the ammonium sulphide contains thiosulphate, the uranyl sulphide is converted into *Uranium-red* $U_6(NH_4)_2SO_9$. This is a fine blood-red coloured amorphous powder, which when heated with caustic potash is converted into the very similar potassium compound $U_6K_2SO_9$, a body which is also formed when uranyl sulphide is heated with potassium hydrosulphide.[2]

503 *Uranous Sulphate*, $U(SO_4)_2+9H_2O$, crystallises from aqueous solution in greenish monosymmetric twinned prisms and

[1] Alibegoff, *Annalen*, 1886, **233**, 117.

[2] Zimmermann, *Annalen*, 1880, **204**, 204.

is isomorphous with crystallised thorium sulphate.[1] In order to prepare this salt the green oxide, U_3O_8, is dissolved in dilute sulphuric acid, and the solution allowed to crystallise after addition of some alcohol. The mother-liquor, which contains uranyl sulphate, yields another crop of crystals of uranous sulphate after it has remained exposed to the light, inasmuch as the uranyl salt present in solution is reduced by the alcohol, and uranous sulphate, being insoluble in dilute alcohol, separates out in crystals containing four molecules of water. Uranous sulphate forms double salts with the sulphates of the alkali-metals ; as, for instance, $U(SO_4)_2+K_2SO_4+H_2O$, and $U(SO_4)_2+(NH_4)_2SO_4+H_2O$.

Uranyl Sulphate, $UO_2SO_4+3H_2O$, is obtained by heating uranyl nitrate with sulphuric acid, and does not crystallise readily. When dissolved in moderately concentrated sulphuric acid, fine yellowish-green fluorescent crystals of $UO_2SO_4+H_2SO_4$ are deposited on cooling, whilst from a solution in concentrated sulphuric acid crystals of a disulphate, $UO_2S_2O_7$, are deposited, which do not fluoresce. By the gradual oxidation of the pitchblende found in Joachimsthal, several new uranium minerals have been formed. Amongst the more important are certain sulphates, such as uranium-vitriol or johannite, and some basic sulphates.

Uranyl sulphate forms double salts with the sulphates of the alkali metals, such as $UO_2SO_4+K_2SO_4+2H_2O$. This is very soluble, and crystallises in yellow crusts, whilst the difficultly soluble ammonium salt, $UO_2SO_4+(NH_4)_2SO_4+2H_2O$, is deposited in monosymmetric lemon-coloured prisms.

Uranium and Nitrogen, Phosphorus and Arsenic.

504 *Uranium Nitride.*—Uranium combines directly with nitrogen at 1000°, forming a yellow nitride,[2] the composition of which is not stated. The nitride, U_3N_4, is obtained as a grey or black powder by heating the tetrachloride in ammonia, mixing the product with ammonium chloride, and again igniting in an atmosphere of ammonia.

Uranyl Nitrate, $UO_2(NO_3)_2+6H_2O$. This salt, which is commonly known as uranium nitrate, is prepared by dissolving any

[1] Rammelsberg, *Zeit. Kryst. Min.* **15**, 640.
[2] Moissan, *Compt. Rend.* 1896, **122**, 274.

of the oxides of uranium in nitric acid. It crystallises in fine lemon-yellow fluorescent rhombic prisms, which are soluble in half their weight of water, and deliquesce on exposure.

Uranyl Phosphates.—The normal orthophosphate is not known. When uranic oxide is treated with phosphoric acid, a crystalline powder is obtained which is partially soluble in water, and the solution deposits yellow crystals of the di-hydrogen salt, $UO_2(H_2PO_4)_2+3H_2O$. The residue contains $2UO_2(H_2PO_4)_2+3H_2O$.

Uranyl Ammonium Phosphate, $UO_2NH_4PO_4$, is a greenish-yellow precipitate, insoluble in acetic acid, obtained by adding a soluble phosphate to a solution of uranyl acetate containing sal-ammoniac. This reaction is employed for the volumetric determination of uranium as well as for that of phosphoric acid.

Several double phosphates occur as minerals; thus

$$(UO_2)_2Ca(PO_4)_2+8 \text{ or } 10H_2O,$$

is known as uranochalcite.

Uranyl Arsenates.—Several of these compounds exist as minerals (Winkler). Trögerite has the composition $(UO_2)_3(AsO_4)_2+12H_2O$; walpurgine is a basic arsenate of uranyl and bismuth; uranospinite is an arsenate of uranium and calcium.

Uranium and Carbon.

505 *Uranium Carbide*, U_2C_3, is obtained by strongly heating a mixture of 500 grams of green uranium oxide and 60 grams of charcoal in the electric furnace, and is a crystalline lustrous solid, which scratches rock crystal but not corundum, and has a specific gravity of 11·28 at 18°. It is attacked by fluorine when gently warmed, by chlorine at 350°, and by oxygen at 370°. In contact with water, about one-third of the carbon is evolved as a gaseous mixture containing 0·2–0·7 per cent. of acetylene, 5·0–7·0 per cent. of ethylene, 78–81 per cent. of methane, and 13·5–15·0 per cent. of hydrogen, the remainder of the carbon being converted into a mixture of solid and liquid hydrocarbons.[1] When two pieces of the carbide are rubbed together, or even shaken in a bottle, brilliant sparks are given off.

Uranyl Carbonates.—Double salts of uranyl carbonate and alkali carbonates are obtained by precipitating a uranyl salt with an alkali carbonate. The potassium salt, UO_2CO_3+

[1] Moissan, *Compt. Rend.* 1896, **122**, 274.

$2K_2CO_3$, is obtained by dissolving potassium uranate in potassium bicarbonate, and evaporating at a moderate temperature, when the compound is deposited in silky crystalline crusts. Water dissolves at the ordinary temperature seven per cent. of its weight of this salt. The corresponding sodium salt is obtained in a similar way, and possesses similar properties. The ammonium compound, $UO_2CO_3+2(NH_4)_2CO_3$, is prepared by gently warming ammonium uranate with a solution of ammonium carbonate, and separates out on cooling in lemon-yellow small flat monosymmetric prisms. It dissolves at the ordinary temperature in 20 per cent. of water, but is less soluble in water containing ammonium carbonate. The mineral liebigite is an apple-green warty mass, occurring together with other uranium minerals. It is a uranyl calcium carbonate, $UO_2CO_3+CaCO_3+10H_2O$.

Detection and Estimation of Uranium.

506 The uranous salts are green and pass rapidly by oxidation into the uranyl salts, which have a yellow colour, and yield with alkalis or alkali carbonates yellow precipitates of the alkali uranates.

In the general separation of the metals uranium is obtained together with iron. In order to separate these, the precipitated oxides are washed and treated with a concentrated solution of ammonium carbonate, and filtered. Uranium is detected in the filtrate after supersaturation with hydrochloric acid, by the brown precipitate produced with ferrocyanide of potassium. When a uranium compound is fused with microcosmic salt in the oxidising flame, a yellow bead is obtained which on cooling becomes green, and on re-heating attains a darker green colour.

Most of the uranyl salts show a strong fluorescence, and give a characteristic absorption spectrum, which has been examined by Morton and Bolton,[1] whilst the fluorescence and phosphorescence spectra have been described by E. Becquerel[2] and H. Becquerel.[3]

In order to determine uranium quantitatively it is converted into the uranyl salt, precipitated with ammonia, and the washed precipitate converted by ignition into the green oxide. It may, like iron, be determined volumetrically with a solution of potas-

[1] *American Chemist*, **3**, 360, 401 ; see also Vogel, *Ber.* 1875, **8**, 1535 ; 1878, **11**, 915 ; Zimmermann, *Annalen*, 1882, **213**, 285.

[2] *Compt. Rend.* 1872, **75** ; 1879, **88**, 1237.

[3] *Compt. Rend.* 1885, **101**, 1252.

sium permanganate, the uranyl compound being previously reduced to the uranous salt by the action of zinc and sulphuric acid, or the solution of uranyl acetate may be precipitated by sodium phosphate.

The uranium phosphates do not impart any tint to the non-luminous gas flame. The spark spectrum of uranium is a complicated one, and has been mapped by Thalén. It consists of a large number of lines, of which a series of five in the green are conspicuous by their brightness, viz., w.l. 5495, 5482, 5480, 5478, and 5475; also three specially bright in the more refrangible portions, viz., 4473, 4363, and 4341.

The *atomic weight* of uranium was determined by Péligot by the analysis of the tetrachloride which he found to contain 37·2 per cent. of chlorine, whence he calculated the number 237·6 as the atomic weight. He afterwards obtained the number 238·3 by the conversion of the acetate, $UO_2(C_2H_3O_2)_2+H_2O$, into the dioxide. Zimmermann, on the other hand, by the same method, obtained the number 237·7, whilst from a series of experiments in which he converted the dioxide into the green oxide and *vice versâ* the number 237·8 was found as the result of many well-agreeing experiments.[1] (O = 15·88.)

GROUP VII.

Fluorine.	Manganese.
Chlorine.	Bromine.
Iodine.	

507 In the periodic system, manganese is the only metallic representative of the even series of the seventh group as yet known, the typical elements of which are fluorine and chlorine, and the remaining members bromine and iodine.

The halogen elements have already been described in vol. i. The analogy of manganese with these elements is almost entirely confined to the derivatives of its highest oxide, Mn_2O_7. To this oxide corresponds permanganic acid, $HMnO_4$, the salts of which are isomorphous with the perchlorates.

In its general chemical behaviour, however, manganese shows strong resemblances to both chromium and iron, between which it stands in the fourth horizontal series. Like chromium it forms a

[1] *Annalen*, 1885, 213, 209.

dioxide, RO_2, and an acidic trioxide, RO_3, and the potassium salt of the acid corresponding to the latter crystallises in the same forms as potassium sulphate and chromate. Both this oxide and the salts are, however, much less stable than the corresponding chromium compounds. On the other hand, manganese resembles iron in forming three oxides of the types RO, R_2O_3, R_3O_4, and two series of salts corresponding to the first two of these. The manganic salts are, however, very unstable, whilst the manganous salts are much more permanent than the salts of iron which contain that metal in the ferrous form.

MANGANESE, Mn = 54·6.

508 Black oxide of manganese, manganese dioxide, or pyrolusite, was known in early times, but for a long period this compound was confounded with magnetic iron ore, and this fact explains the statement of Pliny that loadstone was employed in the manufacture of glass for the purpose of removing or attracting the impurities or colouring matters out of the glass. He distinguished moreover several kinds of magnes; one of these, which is of the feminine gender, does not attract iron: "magnes qui niger est et feminei sexus, ideoque sine viribus." This probably was manganese dioxide. The derivation of the word magnet appears to be doubtful. In the middle ages loadstone was distinguished as *magnes* or *magnesius, lapis.* Pyrolusite, however, was termed *magnesia* probably because Pliny had already pointed out the existence of two species of loadstone. Many of the alchemists, however, believed it to be an ore of iron. They likewise mention its use in glass-making, and in the Latin manuscripts of the sixteenth century it is designated by the term *lapis manganensis,* or similar names.

In 1740, Pott, in his treatise entitled "*Examen chymicum magnesia vitrariorum, Germanis Braunstein,*" proved that the black oxide of manganese does not contain iron, and that from it a definite series of salts can be obtained. He did not, however, suggest that it contained a new metal. Scheele's celebrated investigations on manganese were published in the year 1774. In these he showed that the mineral manganese possesses a strong attraction for phlogiston, and that it takes this substance

up, uniting with acids to form colourless salts; this being explained, according to our present views, by the fact that it gives off oxygen. On the other hand, the solutions of manganese which did not contain phlogiston were shown to be coloured. Scheele believed that the earth contained in this mineral resembled lime; but in the above-mentioned year Bergman, founding his deductions upon Scheele's experiments, came to the conclusion that manganese was probably the calx of a new metal, inasmuch as it coloured glass, and its solutions were precipitated by prussiate of potash, these being reactions common to the metallic calces. Gahn was, however, the first to isolate the new metal. In Germany this was called Braunstein-könig or Braunstein-metal. In other languages, in which braunstein was termed *magnesia niger*, in order to distinguish it from *magnesia alba*, the metal was called manganese or manganesium.

Manganese chiefly occurs in nature as the dioxide or pyrolusite, MnO_2. It is also found in the following minerals: braunite, Mn_2O_3; hausmannite, Mn_3O_4; psilomelane, $(Mn,Ba)O + MnO_2$; manganite, $Mn_2O_2(OH)_2$; rhodocrozite or manganese-spar, $MnCO_3$, which also frequently occurs as an isomorphous constituent in ferrous carbonate and other similar minerals. Manganese also occurs as alabanite or sulphide of manganese, MnS; and hauerite, or manganese disulphide, MnS_2. It likewise forms an essential constituent of many other minerals, although only occurring in them in small quantity. Thus, for instance, most silicates contain manganese, which frequently imparts to them their peculiar colour. By means of these minerals the metal manganese passes into the soil, whence it is absorbed in small quantities into the bodies of plants and animals.

509 *Preparation of Metallic Manganese.*—The higher oxides of manganese can only be reduced to manganese monoxide at a red-heat, the metal not being formed either when the oxide is heated alone or mixed with charcoal in a current of hydrogen, until the temperature rises to a white-heat. The original method of preparing the metal, proposed by John,[1] depends upon this fact. Finely-divided oxide of manganese, obtained by the calcination of the carbonate in a covered crucible, is well mixed with carbon, and the mixture formed into a paste with oil; the paste is then introduced into a crucible lined with charcoal, and the upper portion completely filled with powdered charcoal. The crucible is first heated to redness for half-an-hour to solidify the

[1] Gehlen's *Journ. Chem. Phys.* **3**, 452.

mass, after which the cover is carefully luted down, and the whole exposed in a wind furnace for an hour-and-a-half to the highest temperature which the crucible can support without fusing. The regulus thus prepared contains both carbon and silicon derived from the ashes of the wood charcoal. By igniting the metal a second time in a charcoal crucible with some borax it was obtained by John in a more fusible and brilliant state, and so free from carbon that it left no black residue when treated with an acid.

Deville's [1] method consists in mixing red manganese oxide, Mn_3O_4, prepared by heating the artificial dioxide, with sugar charcoal insufficient in quantity for complete reduction. The mixture is placed in a doubly-lined crucible and heated to whiteness. The regulus obtained is coated with a violet crystalline mass which appears to be calcium-manganese spinelle, CaO,Mn_2O_3.

Hugo Tamm [2] suggests the following as the best method of preparation on the large scale. A flux is prepared of twenty parts of powdered soda-lime glass and seven parts of fluor-spar; six parts of this mixture are then added to one part of lampblack and eleven parts of powdered black oxide of manganese. The mass is heated in a plumbago crucible which has been lined with a mixture of three parts of graphite and one part of fire-clay, and this is then intensely ignited in a wind furnace. A green slag termed "green flux" is obtained in this operation, together with metallic manganese, and this flux serves for a fresh operation. Seven parts of this flux are mixed with ten parts of the best manganese dioxide, one part of lampblack, and some oil. The mass is brought into a similar crucible, covered with a thick piece of wood, and the cover luted down, a small opening being left for the escape of the gases which are evolved. It is first heated gently and then ignited at a white-heat for several hours. In this way four parts of impure manganese metal are obtained, which is found to be covered with a grey slag; the latter may be employed for further melting operations, especially if some of the first flux be added.

This impure manganese, termed cast-manganese, contains a variety of impurities. A specimen of pyrolusite containing 50·5 per cent. of manganese, and 3·5 per cent. of iron gave a regulus having the composition given in column I; after fusion·

[1] *Ann. Chim. Phys.* 1856 [3], **46**, 182.
[2] *Chem. News*, 1872, 111.

with half its weight of manganese carbonate the above regulus yielded a product possessing the composition given in column II.

	I.	II.
Manganese	96·90	99·910
Iron	1·05	0·050
Silicon	0·85	0·015
Carbon	0·95	0·025
Aluminium	0·10	—
Calcium	0·05	—
Phosphorus	0·05	—
Sulphur	0·05	—
	100·00	100·000

Jordan[1] describes a method of preparing metallic manganese on a large scale by treating manganese ores in a blast furnace. The metal obtained is cast-manganese, containing eighty-five per cent. of manganese, six per cent. of carbon, eight per cent. of iron, and traces of silicon, sulphur, and phosphorus.

Other processes of preparing the metal consist in igniting a mixture of fluor-spar and chloride of manganese with metallic sodium,[2] or gradually adding 15 gr. of metallic magnesium to a fused mixture of 100 gr. of manganese chloride and 200 gr. of potassium chloride.[3] The metal may also be obtained by the electrolysis of a concentrated solution of the chloride according to the process described by Bunsen,[4] or by heating the amalgam, which can be prepared electrolytically.[5] An impure metal, containing 4·5 per cent. of carbon, is formed when the oxide is heated with carbon in the electric furnace.[6]

Properties.—Pure manganese, obtained by the reduction process, is a grey or reddish-white metal, having the colour and appearance of cast-iron. It is very hard and brittle, has a specific gravity of about 8·0, and oxidises so easily in the air that it must be kept under rock-oil or in well-sealed vessels. Cast-manganese containing iron is, however, unalterable in the air. Manganese is extremely soluble in all dilute acids, and decomposes water with evolution of hydrogen even in the cold, more rapidly when heated. It melts at a white-heat, and volatilises readily at the temperature of the electric furnace.

[1] *Compt. Rend.* 1878, **86**, 1374.
[2] Brunner, *Pogg. Ann.* 1857, **101**, 264.
[3] Glatzel, *Ber.* 1889, **22**, 2857.
[4] *Pogg. Ann.* 1854, **91**, 619
[5] Prelinger, *Monatsh.* 1894, **14**, 353.
[6] Moissan, *Compt. Rend.* 1893, **116**, 349.

Alloys of Manganese.

510 The alloys of manganese and copper closely resemble those of tin and copper.[1] Those which contain from five to eight per cent. of manganese are malleable, but those in which a higher percentage of manganese is present become grey and brittle. Alloys of manganese, copper, and zinc closely resemble German silver, and may serve as a substitute for this substance.[2] They are obtained by melting mixtures of the oxides with carbon.

Manganese Amalgam is prepared by electrolysing a saturated solution of manganous chloride, mercury being used as the negative pole. When the pasty mass which is obtained is strained and strongly compressed, it yields a slate-coloured mass of specific gravity 12·828, which has the composition Hg_5Mn_2 (Prelinger).

Manganese bronze is made by fusing copper with ferromanganese, and is used for making ships' propellers.

The alloys of manganese and iron, ferromanganese and spiegeleisen, will be described under iron.

COMPOUNDS OF MANGANESE.

Manganese and Oxygen.

511 Manganese forms a series of oxides, of which the following are the best defined:—

Manganese monoxide, MnO.
Trimanganese tetroxide, Mn_3O_4.
Manganese sesquioxide, Mn_2O_3.
Manganese dioxide, MnO_2.
Manganese trioxide, MnO_3.
Manganese heptoxide, Mn_2O_7.

The first of these is a powerful basic oxide, whilst the sesquioxide is feebly basic, giving rise to an unstable series of salts, and the oxide, Mn_3O_4, behaves in many respects as a compound or mixture of the two. The dioxide acts as a weak acidic oxide

[1] Valenciennes, *Compt. Rend.* 1870, **70**, 607.
[2] Allen, *Chem. News*, 1870, **22**, 194.

yielding salts known as the manganites with strong bases. Manganese trioxide and the heptoxide are well-marked acid-forming oxides. The manganates, derived from manganic acid, H_2MnO_4, are very unstable, and as already mentioned are isomorphous with the sulphates and chromates. Permanganic acid, $HMnO_4$, is a strong acid and yields stable salts, which are isomorphous with the perchlorates. The substance described by Franke as the tetroxide, MnO_4, does not appear to exist (Thorpe and Hambly).

Manganese Monoxide, or *Manganous Oxide*, MnO, is best prepared by fusing together a mixture of equal parts of anhydrous manganese chloride and sodium carbonate, to which some sal-ammoniac has been added, and lixiviating the fused mass with water.[1] It is also obtained when a higher oxide or the carbonate is ignited in a current of hydrogen. Manganous oxide is a greyish-green powder, which fuses at a white-heat without loss of oxygen. It has a specific gravity of 5·09. When the powdered oxide is heated in an atmosphere of hydrogen containing a very small quantity of hydrochloric acid, it is obtained crystallised in transparent regular octohedra of an emerald-green colour and an adamantine lustre.[2] It has been found in Sweden as the crystalline mineral manganosite.

Manganous Hydroxide, $Mn(OH)_2$, is obtained as a white precipitate when caustic alkali is added to the solution of a manganese salt. As it oxidises rapidly in the air and assumes a brown colour, forming the oxide Mn_3O_4 and finally Mn_2O_3, it must be precipitated in an atmosphere free from oxygen, and dried at a moderate heat in a current of hydrogen gas. The powder thus obtained is frequently pyrophoric, and when touched with a piece of red-hot charcoal it begins to glow at the point of contact, the oxidation proceeding rapidly throughout the mass. It occurs in Sweden as the mineral pyrochroïte.

The manganous salts, MnR'_2, are usually faintly pink-coloured, although, according to some chemists, this coloration is due to the presence of a trace of a manganic compound. The halogen salts, nitrate and sulphate are readily soluble in water.

Mangano-Manganic Oxide, Red Oxide of Manganese, or *Trimanganese Tetroxide*, Mn_3O_4, occurs with other manganese ores, and also by itself as the mineral hausmannite. This mineral crystallises in acute quadratic pyramids, and one of its best

[1] Liebig and Wöhler, *Pogg. Ann.* 1830, **21**, 584.
[2] Deville, *Compt. Rend.* 1861, **53**, 199.

localities is Ilmenau in Thuringia. Its specific gravity is 4·85. If manganese monoxide be heated in contact with air, or if the higher oxides be strongly heated either in contact or out of contact with air, this same compound is obtained in the form of a brownish-red powder, which then has a specific gravity of 4·72, and is converted into crystals of hausmannite by gently heating it in a slow current of hydrochloric acid.[1] It is also obtained in the crystalline form by heating a mixture of sulphate of manganese and potassium sulphate to bright redness,[2] or by treating a mixture of manganous oxide and calcium chloride in the same way.[3] This oxide dissolves in cold concentrated sulphuric acid, giving rise to a red solution containing a mixture of manganous and manganic sulphates. Hence the red oxide is often considered to be a compound having the formula MnO,Mn_2O_3 or $2MnO,MnO_2$. Thus in many respects it behaves in a similar way to the red oxide of lead; on heating with dilute sulphuric acid, for example, manganous sulphate and manganese dioxide are formed, and boiling nitric acid decomposes it in a manner similar to that in which it acts on red-lead:

$$Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

Chlorine gas is given off when this oxide is heated with hydrochloric acid, and manganous chloride is formed:

$$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + Cl_2.$$

Manganic Oxide or *Manganese Sesquioxide*, Mn_2O_3—This oxide occurs as the mineral braunite crystallised in obtuse quadratic pyramids. It possesses a sub-metallic lustre, has a dark brownish-black colour, and a specific gravity of 4·75. It may be obtained artificially by igniting any of the oxides of manganese in oxygen or in a mixture of this gas and nitrogen, which does not contain more than twenty-six per cent of oxygen.[4] It then forms a black powder, having a specific gravity of 4·32.

Manganic Hydroxide, MnO(OH), occurs in nature as manganite in steel-grey or arsenic-black crystals, belonging to the quadratic system, and having a specific gravity of 4·3. It is usually accompanied by other manganese ores, together with calc-spar and heavy-spar. In general appearance it closely resembles

[1] Deville, *Compt. Rend.* 1861, **53**, 199.
[2] Debray, *Compt. Rend.* 1861, **52**, 985.
[3] Kuhlmann, *Compt. Rend.* 1861, **52**, 1283.
[4] Dittmar, *Journ. Chem. Soc.* 1864, 294.

pyrolusite (manganese dioxide), but it may be distinguished from this compound by its giving a brown instead of a black streak when rubbed on an unglazed porcelain plate. When the mineral is heated at 270–310° in the air it is converted without change of form into the dioxide.[1] Manganic hydroxide is formed when manganous hydroxide is allowed to oxidise in moist air. It may also be prepared by passing chlorine into water in which an excess of manganese carbonate is suspended, or by decomposing the corresponding sulphate with water. It forms a dark brown powder capable of soiling very strongly, and gives off its water at a temperature above 100°. It dissolves in hot nitric acid with formation of manganous nitrate and manganese dioxide :

$$2MnO(OH)+2HNO_3=Mn(NO_3)_2+MnO_2+2H_2O.$$

From this reaction it would appear that in constitution this body resembles lead sesquioxide and analogous compounds having the constitution $MnO.MnO_2$, but in other reactions it acts as a feebly basic oxide, whose salts, with a few exceptions, are very unstable.

The manganic salts, MnR'_3,$Mn_2R''_3$, are extremely unstable and are strongly coloured substances. Only the fluoride, sulphate and a few derivatives of phosphoric acid have been isolated. The sulphate can replace aluminium sulphate in the alums.

Manganese Dioxide and the Manganites.

512 *Manganese Dioxide*, *Manganese Peroxide*, or *Black Oxide of Manganese*, MnO_2, is the most important ore of manganese. It occurs in rhombic crystals and in crystalline and amorphous masses, being known to the mineralogist as pyrolusite. It possesses a metallic lustre, an iron-black or dark steel-grey colour, and a black streak. It is opaque and rather brittle, and has a specific gravity of 4·82. The most celebrated localities for this mineral are Ilmenau in Thuringia, near Platten in Bohemia, near Mährisch-Trubau in Moravia, on the Lahn, and in the Caucasus, France, Spain, and North America. It occurs in the United States, abundantly at Vermont, and in Red Island Bay at San Francisco; and also in New Brunswick and Nova Scotia. It is likewise found in Devonshire. Pyrolusite seldom occurs in the pure state, being generally mixed with other manganese ores such as psilomelane, $(Mn,Ba)O+2MnO_2$, and manganite. It also almost always contains ferric oxide, silica, lime, carbonic

[1] Gorgeu, *Compt. Rend.* 1888, **106**, 1101.

acid and traces of the oxides of cobalt and nickel. Pure manganese dioxide is obtained artificially by melting about 600 grms. of the crystallised nitrate and warming until red fumes appear; the clear liquid is then decanted from the lower oxides which first separate out, and heated in another vessel at 150–160° for 40–60 hours.[1] If manganous carbonate be heated to 260° in presence of air, and the residue then treated with very dilute cold hydrochloric acid, pure manganese dioxide remains behind (Forchhammer).

It appears to be almost impossible to prepare perfectly pure hydrated manganese peroxide,[2] since this substance very readily loses a portion of its oxygen, forming mixtures of the composition $xMnO+yMnO_2$, and moreover readily combines with bases forming manganites. Thus the oxide formed by the reduction of permanganic acid by manganese sulphate, and by the decomposition of permanganic acid in presence of hydrated manganese dioxide, varies in composition from $5MnO_2+MnO$ to $15MnO_2+MnO$. A similar oxide may also be prepared by precipitating a manganese solution with an alkaline solution of a hypochlorite, by treating manganic hydroxide with hot nitric acid,[3] or by adding potassium permanganate to sodium thiosulphate solution. The hydroxide thus obtained, after washing with water, is soluble in water, yielding a brown solution to which the name of manganous acid has been given. This solution turns blue litmus paper red, and does not undergo alteration on standing for many weeks, but small quantities of acid or alkali produce an instant precipitation. Manganese dioxide, like lead dioxide, possesses at the same time feebly basic and feebly acid properties. It is formed when barium manganate is digested with manganese sulphate, and hence, according to Spring, may be regarded as manganese manganate, $Mn.MnO_4$.[4]

The Manganites. — Manganese dioxide combines with several basic oxides to form compounds which may be considered as salts of manganous acid. The composition of these compounds seems to depend on the amount of alkali which is present. A large number of them has been described. *Potassium Manganite*, $K_2Mn_5O_{11}$, is obtained as a yellow precipitate when carbon dioxide is passed into a solution of potassium manganate

[1] Gorgeu, *Bull. Soc. Chim.* 1890 (3), **4**, 16.
[2] Gorgeu, *Compt. Rend.* 1890, **110**, 1134.
[3] Gorgeu, *Ann. Chim. Phys.* 1862 [3], **66**, 155.
[4] *Bull. Soc. Chim.* 1890 [3], **3**, 4.

K_2MnO_4. *Calcium Manganite*, $CaMn_5O_{11}$, is a blackish-brown precipitate formed when a solution of manganous nitrate is poured into an excess of bleaching-powder solution.

Manganese dioxide has long been used for the preparation of colourless glass, and hence pyrolusite has been known as *savon des verriers*. Its mineralogical name, indeed, has reference to this employment of the mineral (from πῦρ, fire, and λύω, I wash). It also serves for the preparation of the manganese compounds and of oxygen, but by far the largest quantity of the mineral is employed for making chlorine, used in the manufacture of bleaching-powder.

513 *Regeneration of Manganese Dioxide from the Chlorine Residues.*—Before the year 1856, the whole of the manganese chloride obtained in the manufacture of chlorine from manganese dioxide and hydrochloric acid was allowed to run to waste. In 1821, Forchhammer[1] observed that when manganous carbonate is heated to 260° in an open vessel it is converted into dioxide. Charles Dunlop[2] applied this reaction to the regeneration of manganese dioxide from the chlorine still-liquors. The free acids which these liquors contain are first neutralised with calcium carbonate, the ferric chloride being at the same time decomposed; the clear liquor is drawn off from the deposited ferric hydroxides, and again treated with calcium carbonate in closed boilers under a pressure of several atmospheres. Under these circumstances the whole of the manganous chloride is converted into the carbonate:

$$MnCl_2 + CaCO_3 = MnCO_3 + CaCl_2.$$

The precipitated carbonate is then separated by subsidence, well washed, and brought on to trays on wheels, which are placed in an oven so that the manganous carbonate is exposed to the action of a current of hot air for forty-eight hours. At the end of this time the carbonate is converted into a black powder which contains about 72 per cent. of MnO_2. In 1857 this process was adopted by Messrs. Charles Tennant and Co., at St. Rollox, and applied to the regeneration of the whole of their manganese, amounting to about 10,000 tons per annum. The process is, however, somewhat costly, and has not been adopted generally by manufacturers of bleaching powder.

A much more perfect and less troublesome process was in-

[1] *Ann. Phil.* 1808, **17**, 50.

[2] *Report of Patent Inventions*, March, 1856, p. 236.

vented by Walter Weldon, in 1867, and first practically carried out at Messrs. Gamble's works at St. Helens, in 1868. This

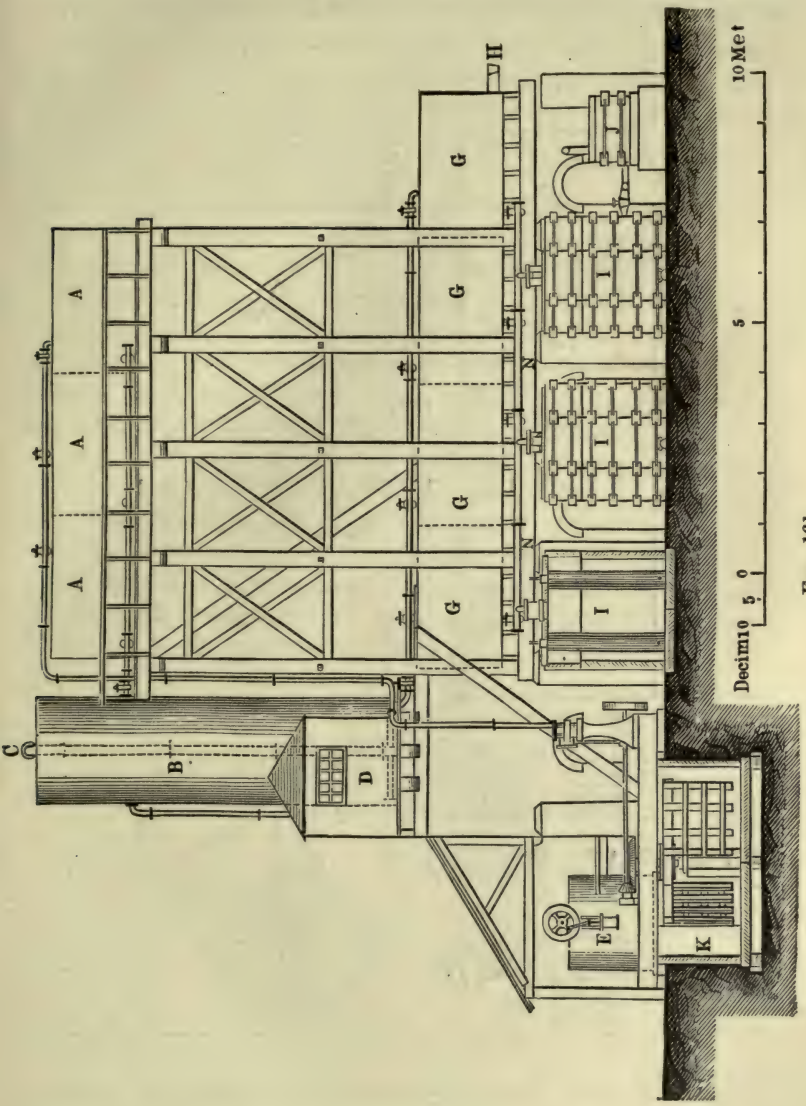


FIG. 161.

process, which is now universally adopted both by British and Continental manufacturers, depends upon the fact that manganous hydroxide is completely transformed into dioxide

by air heated to 55° when an excess of lime is present. The solution of manganese chloride freed from iron and excess of acid by means of calcium carbonate is mixed with milk of lime in 1·6 times the quantity needed for the exact precipitation

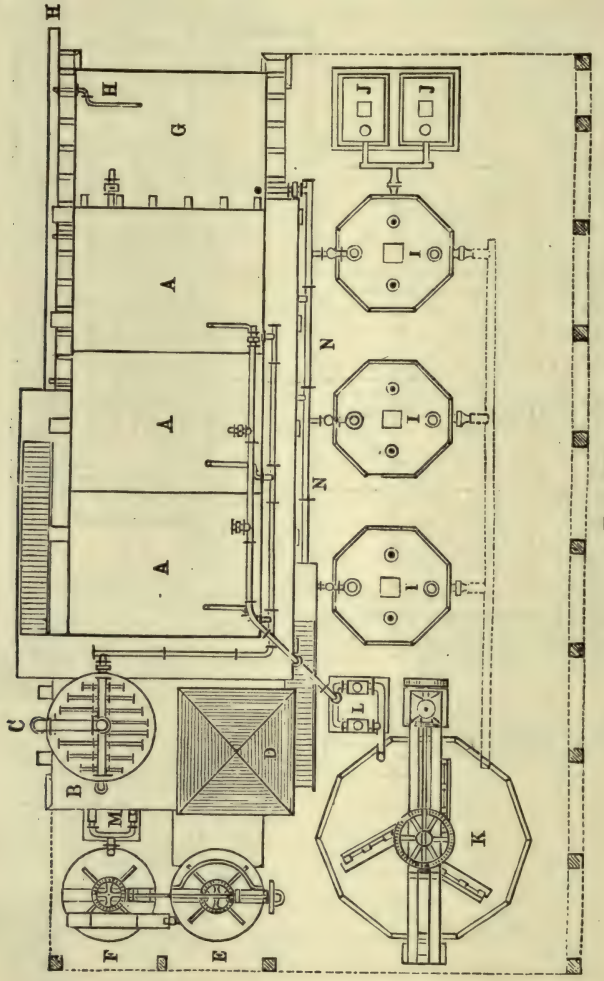


Fig. 162.

of the hydroxide. The resulting mixture, consisting of manganous hydroxide, calcium carbonate, and calcium chloride, is heated by a current of steam to 55°, and a rapid current of air is blown through the liquor. As soon as about three-quarters of the manganous oxide has been transformed into dioxide the liquor

is allowed to settle, and the clear solution of calcium chloride drawn off from the deposit of black dioxide combined with lime, technically termed "manganese-mud."

Fig. 161 exhibits an elevation of an improved form of Weldon plant; Fig. 162 shows the same in plan; K is the well in which the liquor which runs from the chlorine stills I, I, I, and J, J, is neutralised with lime-stone. This liquor is then pumped up by means of the pump L into the still-liquor settlers A, A, A, in which the oxide of iron is deposited. From the settlers the neutral chloride of manganese solution is run by means of iron pipes into the large oxidiser B; here it is mixed with milk of lime contained in the vessel F, having previously been prepared in the vessel E, and being pumped up into the oxidiser by the pump M. Steam is then passed into the oxidiser filled with the liquor until the right temperature has been attained, and then a blast of air is blown in by means of the blowing-engines through the air-pipe C. After the operation is complete the oxidised liquor is allowed to deposit the mud in the mud-settlers G, G, G, and from these the clear solution of calcium chloride is run off by the pipes H, the manganese-mud passing through the iron pipes N into the chlorine stills, I, I, I. D is a small laboratory in which the necessary tests are made, and J, J are two small stills used for the evolution of chlorine from native manganese in order to supply the small but inevitable loss which takes place.

Manganese Trioxide and Heptoxide, Manganic Acid, Permanganic Acid, and their Salts.

514 In his work entitled *The Prosperity of Germany*,[1] published in 1656, Glauber mentions that when manganese is fused with fixed saltpetre (caustic potash) a mass is produced from which he obtained "a most dainty purple fiery liquor," this afterwards turning blue, red, and green. In 1705 an anonymous treatise appeared, entitled *Key to the Secret Cabinet of Nature's Treasury*; in this it is stated that the product obtained by fusing saltpetre and manganese yields a solution of which the colour alters, first being grass-green, then sky-blue, violet-coloured, and lastly rose-red. The changes of colour which are here given are exactly the opposite of those which Glauber noticed. Pott in

[1] Packe's translation, 1687, p. 353.

1740 described these changes, believing that they had not been previously noticed, and Scheele, who endeavoured to explain these phenomena, gave to the colouring material the name of mineral chameleon, a term which had previously been applied to other mineral colouring matters capable of undergoing changes of tint. The properties of this mineral chameleon were afterwards investigated by many chemists, but it was not until the year 1817, when Chevillot and Edwards[1] investigated the subject, that a rational view of its composition was arrived at. They showed that when much alkali is employed a green compound is formed; that when, on the other hand, an excess of manganese is fused with potash a red body is produced, and they succeeded in preparing the substance obtained by the latter reaction in the crystalline form. They also showed that an absorption of oxygen takes place, and consequently they assumed that the potash-salt forms with manganese a manganate, and that the green salt contains more base than the red. Forchhammer[2] investigated the subject in 1820, and ascribed the difference in colour to the existence of two distinct acids. It is, however, to Mitscherlich[3] that we owe a knowledge of the exact composition of these two acids.

Manganese Trioxide, MnO_3, is a deliquescent amorphous reddish mass, prepared by dropping a solution of potassium permanganate in concentrated sulphuric acid on to dry sodium carbonate:[4]

$$(MnO_3)_2SO_4 + Na_2CO_3 = Na_2SO_4 + 2MnO_3 + CO_2 + O.$$

It is only formed in extremely small quantity, and is carried forward by the carbonic acid as a pink fume, which may be caught on fragments of glass placed in a freezing mixture.

When thrown into water it is decomposed as follows (Thorpe and Hambly):[5]

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2$$

The *Manganates* have a green colour, and their solutions are only stable when they contain large quantities of free alkali. If carbon dioxide be passed through them, or if they be diluted with much water or acidified, the liquid passes from a green to

[1] *Ann. Chim. Phys.* 1817 [2], **4**, 287.
[2] *Ann. Phil.* 1807, **16**, 130; 1808, **17**, 150.
[3] *Pogg. Ann.* 1832, **25**, 287.
[4] Franke, *J. pr. Chem.* 1887 (2), **36**, 893.
[5] *Journ. Chem. Soc.* 1888, i. 175.

a blue and violet colour, the permanganate being formed, and the dioxide deposited:

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KHO.$$

The manganates are also converted by direct oxidation into permanganates when they are dissolved in a large quantity of water containing dissolved oxygen.

Manganates are produced by the partial reduction of permanganates in alkaline solution; and this change occurs when small amounts of reducing agents such as alcohol and sodium thiosulphate are added to the red alkaline liquid. The latter also gradually turns blue and afterwards green simply on exposure to air, this being caused by the reducing action of the organic matter contained in the atmosphere. These reactions explain the changes of colour of the mineral chameleon.

Potassium Manganate, K_2MnO_4, is formed when manganese dioxide is fused together with caustic potash. If the fusion takes place in the absence of air, the following reaction occurs:

$$3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O.$$

Chevillot and Edwards found, indeed, that when the fusion took place in an atmosphere of nitrogen no manganate was formed. According to Elliot and Storer [1] this depends upon the fact that the manganate is decomposed in a current of nitrogen below a red-heat; whereas at a lower temperature, as at 180°, the manganate remains undecomposed. In the presence of air, or on the addition of nitre or potassium chlorate, a larger quantity of the product is obtained,

$$2KOH + MnO_2 + O = K_2MnO_4 + H_2O.$$

The deep-green coloured mass dissolves in a small quantity of water, forming a dark-green solution, from which, on evaporation in a vacuum, the salt separates out in small crystals isomorphous with those of potassium sulphate.

Sodium Manganate, Na_2MnO_4, is formed when a mixture of equal parts of manganese dioxide and caustic soda is heated for sixteen hours; the mass is then lixiviated with a small quantity of water and the solution cooled down, when the salt separates out in small crystals isomorphous with Glauber's salt, and having

[1] *Proc. Am. Acad. Art. Sci.* **5**, 192.

the composition $Na_2MnO_4+10H_2O$. These dissolve in water with partial decomposition, yielding a green solution. Sodium manganate is now used largely as a deodoriser.

Barium Manganate, $BaMnO_4$, is formed when manganese dioxide is heated with baryta or barium carbonate or nitrate, or when barium permanganate is heated with baryta water. It is an emerald-green powder, consisting of microscopic four-sided prisms or six-sided plates. It has a specific gravity of 4·85, and is insoluble in water, but readily decomposed by acids. The employment of this salt in place of the poisonous Scheele's green has been suggested,[1] and it has been employed in a few instances, though not so generally as might be wished.

515 *Manganese Heptoxide*, Mn_2O_7, and *Permanganic Acid*, $HMnO_4$.—The first of these compounds, also termed permanganic anhydride, was noticed by Chevillot, and afterwards investigated by Thénard,[2] Aschoff,[3] and Terreil.[4] In order to prepare this compound, pure potassium permanganate free from chlorine is gradually added to well-cooled highly concentrated sulphuric acid. The salt dissolves with an olive-green colour, and if the solution be cooled, and water carefully added, the heptoxide separates as a dark reddish-brown liquid[5] which does not solidify at $-20°$. It is extremely unstable, constantly evolving bubbles of oxygen on exposure to the air. These carry with them a small quantity of the heptoxide, and thus violet fumes are emitted. It rapidly absorbs moisture, and dissolves in water yielding a deep violet-coloured solution, so much heat being thereby evolved that the liquid undergoes partial decomposition. It dissolves in concentrated sulphuric acid with an olive-green colour. On heating, it decomposes, with evolution of light and heat, and with violent explosion. The green solution contains the sulphate $(MnO_3)_2SO_4$:

$$2KMnO_4+2H_2SO_4=(MnO_3)_2SO_4+K_2SO_4+2H_2O,$$

and this on addition of water yields the heptoxide

$$(MnO_3)_2SO_4+H_2O=Mn_2O_7+H_2SO_4.$$

Permanganic Acid, $HMnO_4$, is obtained in aqueous solution by adding the requisite quantity of dilute sulphuric acid to

[1] Schad, *Deutsch Industriezeit.*, 1865, 118; Rosentiehl, *Dingl. Polyt. Journ.* 1865, **177**, 409.
[2] *Compt. Rend.* 1856, **42**, 389.
[3] *Pogg. Ann.* 1860, **111**, 217.
[4] *Bull. Soc. Chim.* 1862, 40.
[5] Franke, *J. pr. Chem.* 1885 [2], **31**, 166.

the barium salt. A deep red liquid is thus obtained, which exhibits a blue colour by reflected light, and possesses a bitter metallic taste. It decomposes on exposure to light, or when heated gently, and still more rapidly when boiled, with evolution of oxygen and separation of the hydrated dioxide. It acts as a most powerful oxidising agent.

Permanganic acid is also formed when manganese nitrate or any manganous salt, with the exception of the haloid compounds, is warmed with nitric acid and lead dioxide.

A weak solution of permanganic acid continually evolves oxygen at a very slow rate. When, however, such a solution is shaken with hydrogen or carbonic oxide, the gas is rapidly absorbed and a considerable volume of oxygen evolved. The exact nature of the change which occurs has not yet been ascertained (Victor Meyer and Recklinghausen).[1]

Potassium Permanganate, $KMnO_4$, is prepared on the large scale by a process which will be described further on. For laboratory purposes it is best obtained according to the process given by Gregory. This consists in dissolving ten parts of caustic potash in the smallest quantity of water, then adding to this a mixture of seven parts of potassium chlorate and eight parts of manganese dioxide, evaporating the whole to dryness, and heating the residue until the potassium chlorate is completely decomposed. The dark-green mass is then lixiviated with boiling water, the solution allowed to deposit, and the liquid filtered through asbestos or gun-cotton. The clear solution deposits the crystals on standing.

Potassium permanganate is isomorphous with potassium perchlorate, with which it crystallises in all proportions. The crystals are almost black, and when freshly prepared possess a green metallic lustre, which however on exposure to the air becomes of a steel-blue tint without any further alteration in the salt taking place. The crystals have a specific gravity of 2·7, and yield a red powder. They dissolve in fifteen to sixteen parts of cold water (Mitscherlich), forming a deep purple-coloured solution. On heating to 240° they decompose as follows:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

Jones[2] has shown that hydrogen and phosphine decompose potassium permanganate, and that oxygen gas is evolved

[1] *Ber.* 1896, **29**, 2549, 2828. [2] *Journ. Chem. Soc.* 1878, i. 95.

together with carbon dioxide when sulphuric acid acts on permanganate in presence of oxalic acid.

Mixed with sulphur or phosphorus, a material is obtained which takes fire or explodes violently on percussion, and a mixture of the salt with charcoal burns like tinder.

Potassium permanganate is largely used as an oxidising agent both in analytical work and for the preparation of many organic oxidation products. In alkaline solution it is first converted into manganate, which afterwards loses a further amount of oxygen and yields the hydrated dioxide, three atoms of the oxygen contained in two molecules of the salt being employed in the oxidation:

$$(1)\ 2KMnO_4 + 2KHO = 2K_2MnO_4 + H_2O + O.$$

$$(2)\ 2K_2MnO_4 + 2H_2O = 2MnO_2 + 4KHO + 2O.$$

It is in this way for example that potassium permanganate acts when it is brought into contact with a hot solution of a manganous salt, the whole of the manganese being precipitated as dioxide; three-fifths of this is therefore formed by the oxidation of the manganese salt added and the remaining two-fifths by the reduction of the permanganate:

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

In acid solution the manganese of the permanganate is finally converted into a salt corresponding to the monoxide, MnO, five atoms of oxygen being rendered available:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Thus, the action of acid potassium permanganate solution on ferrous sulphate, in presence of sulphuric acid, is represented as follows:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

The acid solution of potassium permanganate is reduced by hydrogen peroxide with evolution of oxygen, half of which is due to the reduction of the peroxide, half to that of the permanganate:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Sodium Permanganate, $NaMnO_4$, is obtained in a similar way to the potassium salt, and is distinguished from it by being deliquescent, and, therefore, crystallising with difficulty.

Ammonium Permanganate, NH_4MnO_4, is obtained by the decomposition of the potassium salt with ammonium sulphate. It is isomorphous with potassium permanganate, and decomposes readily on heating.

Barium Permanganate, $Ba(MnO_4)_2$, forms hard, almost black prisms, soluble in water. It is obtained by passing a current of carbon dioxide through water containing barium manganate in suspension, or by the action of barium chloride on silver permanganate.

Silver Permanganate, $AgMnO_4$, separates out in large regular crystals when warm solutions of nitrate of silver and potassium permanganate are mixed. It dissolves in 190 parts of water at 15°, and is much more soluble in warm water. The solution decomposes on boiling.

Condy's Disinfecting Liquid.—Potassium permanganate has been employed for a long time in the laboratory as a powerful oxidising agent, and is largely used in volumetric analysis. Hofmann was the first, in the year 1859, to show that this salt together with the other manganates and permanganates acts as a valuable disinfecting agent, and its application for this purpose has become now so general that these compounds, which at that time were only found in the laboratory, are now made in thousands of tons. For disinfecting purposes it is not necessary to employ the pure, well-crystallised salt which is used in the laboratory, but a commercial article consisting of a mixture, more or less pure, of manganate and permanganate of sodium is used. This substance is obtained by mixing the caustic soda obtained from 1,500 kilos. of soda-ash with 350 kilos. of finely-divided manganese dioxide in a flat vessel, and heating this mixture for forty-eight hours to dull redness. The product, containing about 26 per cent. of pure manganate, is either used in that form, or lixiviated with water, and the solution either boiled down to the requisite degree of strength or evaporated to dryness. If the manganate is to be completely converted into permanganate it is neutralised with sulphuric acid, and the solution concentrated until Glauber's salt separates out; these crystals are then removed and the liquid further evaporated.[1]

[1] Hofmann's *Report Exhib.* 1862, 109.

Manganese and the Halogens.

516 *Manganous Fluoride*, MnF_2, is obtained by dissolving the carbonate in hydrofluoric acid, the compound being deposited on evaporation in distinct amethyst-coloured crystals, which are insoluble in pure water, but dissolve in water containing free hydrofluoric acid.

Manganic Fluoride, MnF_3+3H_2O, is obtained in ruby-red crystals by dissolving the sesqui- or the di-oxide in hydrofluoric acid. It readily forms compounds with the alkali fluorides.[1]

Manganous Chloride, $MnCl_2$, is formed when the metal is burned in chlorine gas, or when hydrochloric acid is passed over heated manganous carbonate. Prepared in this way manganese chloride is a pale rose-coloured mass, having a lamino-crystalline structure. When heated to redness it fuses to an oily liquid, and decomposes in moist air at this temperature with formation of hydrochloric acid and the oxides of manganese. Manganese chloride is obtained in solution by dissolving the carbonate or any of the oxides in hydrochloric acid. For this purpose the residues from the preparation of chlorine by means of pyrolusite and hydrochloric acid may be utilised. These are always coloured yellow, from the presence of ferric chloride, and contain an excess of acid. They must be evaporated to drive off the acid, then diluted with water, and a tenth of the solution precipitated with sodium carbonate. The precipitate, consisting of manganese carbonate and ferric hydroxide, is then well washed with hot water and boiled with the remainder of the liquid. By this means the whole of the iron is precipitated as ferric oxide, and in order to ascertain that the precipitation of the iron is complete, a small portion of the liquid is filtered off and a drop or two of ferrocyanide of potassium added; if free from iron only a white precipitate will be formed; if, however, the precipitate has a bluish colour, iron is still contained in solution, and the liquid requires to be boiled for a longer time with manganese carbonate. The filtrate may contain copper, barium, and calcium. The first of these metals is removed by passing a current of sulphuretted hydrogen through the liquid. If the last two metals are present the manganese is best precipitated by sulphide of ammonium, the precipitate well washed with hot water, and then dissolved in

[1] Christensen, *J. pr. Chem.* 1887 (2), **35**, 57, 161, 541.

hydrochloric acid. On evaporation, the concentrated solution deposits between 15° and 20° light pink-coloured monosymmetric crystals of the hydrated chloride $MnCl_2+4H_2O$. According to Marignac [1] crystals are sometimes obtained of the same composition at a lower temperature; these also belong to the monosymmetric system but are of a different form, being isomorphous with those of hydrated ferrous chloride, $FeCl_2+4H_2O$. The crystals lose two molecules of water when placed over sulphuric acid (Graham),[2] and when heated they fuse at 87·5° to a clear liquid. One hundred parts of water dissolves according to Brandes:

	At 10°	31°	62·5°
$MnCl_2+4H_2O$	150	270	625 parts.

The solubility does not increase above 62·5°, and the concentrated pink solution is syrupy and boils at 106°. This salt is also soluble in alcohol with a green colour, and the alcoholic solution burns on ignition with a red flame. Manganese chloride forms double salts with the chlorides of the alkali metals.

Manganic Chloride, $MnCl_3$, is not known in the solid state. It appears, however, to be formed in solution when either of the oxides Mn_3O_4, Mn_2O_3, or MnO_2, is added to cold concentrated hydrochloric acid.[3] When the dark-brown solution is heated, the manganic chloride is decomposed and chlorine is evolved:

$$2MnCl_3=2MnCl_2+Cl_2.$$

The addition of water to the solution precipitates a portion of the manganese as the hydrated sesquioxide.[4]

Manganese Tetrachloride, $MnCl_4$.—Nicklès obtained a deep-green solution on shaking manganese dioxide with ether saturated with hydrochloric acid. This contains the compound $MnCl_2.MnCl_4$, and when shaken with more ether becomes dark-blue as the tetrachloride is thus extracted. If this be saturated in a freezing mixture with hydrochloric acid, a green oily liquid having the composition H_2MnCl_6 is formed.

Permanganic Oxychloride, MnO_3Cl.—This chloride of permanganic acid was first prepared by Dumas:[5] he did not however

[1] *Compt. Rend.* 1857, **45**, 650.
[2] Compare Sabatier, *Bull. Soc. Chim.* 1894 (3), **11**, 546.
[3] Pickering, *Journ. Chem. Soc.* 1879, i, 654.
[4] Christensen, *J. pr. Chem.* 1887 (2), **35**, 57, 161, 541.
[5] *Ann. Chim. Phys.* 1827 [2], **36**, 81.

analyse the compound, but from its mode of decomposition considered it to be manganese heptachloride, $MnCl_7$. It is obtained by gradually adding fused sodium chloride to a solution of potassium permanganate in concentrated sulphuric acid. A yellow gas is then evolved, which when passed through a freezing mixture condenses to a greenish-brown liquid. This when exposed to the air emits a purple-red vapour, which possesses the peculiar smell of the oxides of chlorine, and like them acts most violently upon the mucous membranes, so that the smallest quantity of the chloride contained in the commercial permanganate can be thus readily detected.[1] When heated it explodes violently, and water decomposes it with formation of permanganio acid and hydrochloric acid. These substances however mutually decompose with formation of free chlorine and manganese dioxide. A corresponding oxyfluoride, MnO_3F, exists, and was first prepared by Wöhler.[2]

Manganous Bromide, $MnBr_2$, is obtained by heating the powdered metal in bromine vapour, and when the compound is fused it is obtained as a pale-red mass. When the carbonate is dissolved in hydrobromic acid the hydrated bromide, $MnBr_2 + 4H_2O$, is obtained, and this has been found by Marignac to be isomorphous with the ordinary form of the chloride.

Manganous Iodide, $MnI_2 + 4H_2O$, is obtained crystallised in colourless deliquescent needles, which become coloured on exposure to air.

Manganese and Sulphur.

517 *Manganese Monosulphide*, MnS, occurs as the mineral manganese-blende, or alabandite, forming a steel-grey crystalline mass with a green streak, and sometimes observed in cubes and octohedra. It has a specific gravity of 4·04, and occurs in veins in the coal-mines in Transylvania, and in Freiberg and Mexico. It may be obtained artificially in the form of a dark-grey powder, which melts at a high temperature forming a steel-grey crystalline mass, by heating the monoxide, the carbonate, or the sulphate in a current of hydrogen sulphide (Arfvedson), or in green octohedra by heating manganous sulphide with a little sulphur in the electric furnace.[3] Ammonium

[1] Aschoff, *Pogg. Ann.* 1860, **111**, 217.
[2] *Pogg. Ann.* 1827, **9**, 619.
[3] Moissan, *Compt. Rend.* 1895, **121**, 202.

sulphide and the other monosulphides of the alkali-metals precipitate anhydrous manganese sulphide from a solution of a manganous salt in the form of a light flesh-coloured precipitate, which dissolves readily in dilute acids and oxidises on exposure to the air, assuming a brown tint. When left in contact with ammonium sulphide, when heated with it to 300°,[1] and when suspended in a dilute solution of sulphuretted hydrogen and exposed to a low temperature, it passes into the green crystalline sulphide.[2]

Manganese sulphide combines with the sulphides of the alkali metals to form salts.[3] The potassium salt, $K_2S+3MnS$, is formed when the anhydrous sulphate of manganese is gradually heated to redness, with three parts of potassium carbonate, 0·2 parts of lamp-black and excess of sulphur. The fused mass is treated with cold water freed from air, when a dark-red crystalline mass remains behind, which appears to consist of transparent micaceous scales. In the dry state this compound is stable, but in the moist state it readily undergoes oxidation, becoming black and opaque, and when heated with nitre a violent explosion occurs.

Manganese Disulphide, MnS_2.—This substance is found as the mineral hauerite in crystals belonging to the regular system. They possess a metallic adamantine lustre, and a reddish-brown colour, and occur at Kalinka in Hungary in clay together with sulphur and gypsum.

Manganous Sulphate, $MnSO_4$, is best prepared by mixing commercial black oxide of manganese to a paste with sulphuric acid and heating the mixture in a crucible to strong redness when the greater part of the iron sulphate is destroyed. The filtrate obtained after lixiviating the residue is then heated with a small quantity of manganous carbonate in order to precipitate the last traces of iron.

It has a specific gravity of 3·1, and is decomposed at a bright red heat, leaving a residue of red oxide of manganese. No less than seven different hydrates can be obtained by crystallising the salt from water at different temperatures. At temperatures above 117° the anhydrous salt separates out, whilst between this temperature and about 60° the monohydrate is deposited. Each of these salts is less soluble in hot than in cold water, and

[1] Antony and Donnini, *Journ. Chem. Soc.* 1893, **2**, ii. 527.
[2] Villiers, *Compt. Rend.* 1895, **120** 322.
[3] Völker, *Annalen*, 1846, **59**, 35; Brunner, *Journ. Chem. Soc.* 1890, ii. 215.

hence solid matter is deposited when a saturated solution is heated. At about 43° the hydrate with $2H_2O$ separates, whilst that with $3H_2O$ is formed as a crystalline crust at about 30°. The salt which crystallises out at the ordinary temperature is the tetrahydrate, and forms transparent rose-coloured prisms of sp. gr. 2·097 (Kopp). At lower temperatures the hydrates with $5H_2O$ (10–15°), $6H_2O$ (2–5°) and $7H_2O$ (—10–5°) are formed. All these hydrates have their own characteristic solubility, which increases with the temperature except in the case of the monohydrate.[1] 100 parts of water dissolve

at	15°	20°	40°
$MnSO_4+4H_2O$	99·1	106·8	117·6

Manganous sulphate is insoluble in absolute alcohol, this liquid removing a portion of the water from the hydrates. Finely crystalline double sulphates are formed when manganous sulphate and the sulphates of the alkali-metals are crystallised together, and these are isomorphous with the corresponding salts formed by magnesium and by copper.

Manganous Aluminium Sulphate, $MnSO_4+Al_2(SO_4)_3+24H_2O$. This substance occurs as the mineral apjohnite found in Algoa Bay in South Africa.[2]

Manganic Sulphate, $Mn_2(SO_4)_3$.—Manganic oxide and hydroxide dissolve with difficulty in sulphuric acid. The red oxide Mn_3O_4, on the other hand, dissolves readily, yielding a purple-red-coloured solution. If the finely-divided precipitated dioxide be treated with sulphuric acid, oxygen is evolved, and at a temperature of 138° a green liquid is obtained from which the sulphate is precipitated as a non-crystalline powder. In order to purify this salt it is brought on to a porous porcelain plate, when the greater part of the sulphuric acid is absorbed; the residue is then washed with pure nitric acid and the salt allowed to dry in absence of air on another porous plate, and then heated to 150°.[3]

Manganic Potassium Sulphate, or *Manganese Alum*, $K_2SO_4+Mn_2(SO_4)_3+24H_2O$.—This is obtained when potassium sulphate is added to a solution of the foregoing salt containing an excess of sulphuric acid. On evaporation to a syrupy consistency the

[1] Linebarger, *Amer. Chem. Journ.* 1893, **15**, 225.
[2] *Phil. Mag.* 1856 (3), **12**, 103.
[3] Carius, *Annalen*, 1856, **98**, 53.

above salt crystallises out in violet-coloured regular octohedra; it is decomposed in contact with water with separation of manganic hydroxide.

Manganese Ammonium Alum, $(NH_4)_2SO_4 + Mn_2(SO_4)_3 + 24H_2O$. —This salt corresponds closely to the above-mentioned potassium compound, and is obtained in a similar way. Anhydrous ammonium manganese alum has also been obtained and forms violet crystals which are decomposed by water.[1]

Manganous Dithionate, $MnS_2O_6 + 3H_2O$.—This salt is of interest inasmuch as it is employed for the preparation of dithionic acid (vol. i, 415). It is obtained by passing sulphur dioxide through water in which finely-divided manganese dioxide is suspended. The solution always contains a small quantity of manganese sulphate, and for this reason baryta water is added as long as a precipitate is formed. Manganese dithionate is deposited in easily soluble rhombohedral crystals.

Manganese and the Elements of the Nitrogen Group.

518 *Manganese Nitride.*—The compound Mn_5N_2 is produced when nitrogen is passed over finely-divided manganese at a red heat. When ammonia is substituted for nitrogen, the substance formed has the composition Mn_3N_2. Both of these form dark coloured powders which yield ammonia when they are heated in hydrogen or fused with potash.[2]

Manganous Nitrate, $Mn(NO_3)_2 + 6H_2O$, crystallises with difficulty in white deliquescent needles which readily dissolve in alcohol. The salt melts on heating, and the liquid boils at 129·5°, at which temperature a black deposit of manganese oxides is formed.

Manganese Phosphide, Mn_3P_2, is obtained in slender needles when manganese chloride is heated in a current of hydrogen saturated with phosphorus vapour. It dissolves in aqua regia, but not in nitric acid.[3]

Manganous Phosphates.—These salts have been investigated by Heintz,[4] Debray,[5] Bödecker,[6] and Erlenmeyer.[7] The normal manganous orthophosphate, $Mn_3(PO_4)_2 + 7H_2O$, is a white

[1] Lepierre, *Compt. Rend.* 1895, 120. [2] Prelinger, *Monatsh.* 1894, **15**, 391.
[3] Granger, *Compt. Rend.* 1897, **124**, 190.
[4] *Pogg. Ann.* 1848, **74**, 450. [5] *Annalen*, 1849, **69**, 208.
[6] *Ann. Chim. Phys.* 1861 [3], **61**, 433.
[7] *Annalen*, 1877, **190**, 191.

imperfectly crystalline precipitate. The monohydrogen salt, $HMnPO_4+3H_2O$, forms small prismatic rose-coloured rhombic crystals slightly soluble in water, and the dihydrogen phosphate, $H_4Mn(PO_4)_2+2H_2O$, crystallises in red four-sided prisms which deliquesce on exposure to the air, decomposing into free phosphoric acid and the preceding salt.

Manganic Phosphates.—Both manganic oxide and the dioxide dissolve in a concentrated solution of phosphoric acid, in the latter case with evolution of oxygen, with formation of a deep violet liquid, from which a violet-coloured crystalline mass separates out (Gmelin). This decomposes in contact with water, and manganic hydroxide is precipitated from the solution by the alkalis. On evaporating the red solution a peach-blossom coloured powder separates, consisting of manganic metaphosphate, $Mn(PO_3)_3+H_2O$.[1] The normal phosphate, $MnPO_4+H_2O$, an acid pyrophosphate, $MnHP_2O_7$, and the salt $MnKP_2O_7$, have also been prepared.[2]

Manganous Arsenate.—When arsenic acid is saturated with manganese carbonate, a difficultly soluble salt having the composition $HMnAsO_4$ is formed. This dissolves readily in arsenic acid with formation of the salt $H_4Mn(AsO_4)_2$, which latter crystallises in rectangular plates.

Several double salts with the alkali arsenates are also known.[3]

Manganese and the Elements of the Carbon Group.

519 *Manganese Carbide*, Mn_3C, is formed when red oxide of manganese is heated with charcoal in the electric furnace. It has the sp. gr. of 6·89, and when treated with water it yields equal volumes of hydrogen and marsh gas:

$$Mn_3C+6H_2O=CH_4+H_2+3Mn(OH)_2.$$

It readily burns in oxygen and is easily attacked by fluorine and chlorine.[4]

Manganous Carbonate, $MnCO_3$, forms an isomorphous constituent of chalybite and dolomite, and also occurs in the pure state in the rose-red crystals of manganese spar or rhodochro-

[1] Hermann, *Pogg. Ann.* 1848, **74**, 303.

[2] Christensen, *J. pr. Chem.* 1883 (2), **28**, 1; Schjerning, *J. pr. Chem.* 1892 (2), **45**, 515.

[3] Lefèvre, *Compt. Rend.* 1890, **110**, 405.

[4] Moissan, *Compt. Rend.* 1896, **122**, 421.

zite. All these minerals crystallise, like calc-spar, in rhombohedra, but manganocalcite, $(Mn,Ca,Mg)CO_3$, is isomorphous with arragonite.

The hydrated manganese carbonate is obtained as a white precipitate by mixing a solution of the chloride or sulphate of manganese with sodium carbonate. In the moist state it soon becomes brown coloured on exposure to the air; it dissolves in 8,000 parts of pure water, and in about half the quantity of water saturated with carbon dioxide.

Manganese and Cyanogen.—When a concentrated solution of acetate of manganese is warmed with solid potassium cyanide, a green precipitate is thrown down of $KCN,Mn(CN)_2$; this gradually disappears, and in its place dark blue crystals of potassium mangano-cyanide, $K_4Mn(CN)_6+3H_2O$, are formed.[1] The mangano-cyanide is also obtained when manganous carbonate is heated to a temperature of from 40° to 50° with a solution of cyanide of potassium.[2] The salt crystallises in deep violet-blue quadratic efflorescent tables. Its solution oxidises on exposure to air with formation of potassium mangani-cyanide, $K_3Mn(CN)_6$, which crystallises in dark-red prisms. This latter salt when brought into contact with potassium amalgam in aqueous solution is again transformed into mangano-cyanide. The constitution of these compounds, which are not merely double salts, will be referred to under the corresponding iron compounds.

Manganese Silicide, Mn_2Si, is formed when the two elements are heated together in the electric furnace and is a very hard brittle mass, which has a metallic lustre and steel grey colour and a sp. gr. of 6·6. It is not decomposed by water at the ordinary temperature, but it is attacked by steam, oxygen and chlorine at a red heat. Fluorine decomposes it at the ordinary temperature.[3]

Manganous Silicates occur as isomorphous constituents of many minerals. Some naturally occurring manganese silicates are known. Thus, for instance, rhodonite, $MnSiO_3$, occurs in light brownish-red transparent asymmetric crystals, and tephroite, Mn_2SiO_4, crystallises in the quadratic system in rose-red, brown, or grey masses, and usually occurs together with rhodonite.

[1] Eaton and Fittig, *Annalen*, 1868, **145**, 157.
[2] Decamps, *Ann. Chim. Phys.* 1881 [5], **24**, 178.
[3] Vigouroux, *Compt. Rend.* 1895, **121**, 771.

Manganese and Boron.

520 *Manganese Borate,* $MnH_4(BO_3)_2$, is formed as an almost white powder when manganese sulphate is added to a solution of borax, and the precipitate dried at 100°. When it is heated to redness it yields the metaborate, $Mn(BO_2)_2$. The precipitated salt is used in the preparation of drying oils and oil varnishes.[1]

Detection and Estimation of Manganese.

521 Manganese is distinguished by forming a flesh-coloured sulphide readily soluble in dilute acids. In the course of analysis manganese is thrown down with the sulphides and hydroxides of the metals which are precipitated by sulphide of ammonium. If the precipitate be treated with very dilute cold hydrochloric acid, the sulphides of cobalt and nickel, if present, remain undissolved. The solution is heated with potassium chlorate in order to remove the sulphuretted hydrogen, and an excess of caustic soda is added. Iron, manganese, and uranium are thus thrown down as hydroxides. The washed precipitate is then dissolved in hydrochloric acid, and the liquid neutralised with ammonia, and ammonium chloride added, when the whole of the metals, with the exception of manganese, are thrown down and the filtrate is then evaporated to dryness, and the residue heated to get rid of ammoniacal salts. The mass which remains can be treated in various ways for the detection of manganese. The simplest plan is to fuse a small quantity of the residue with caustic soda and saltpetre, when the dark-green potassium manganate is formed, and this colour becomes deep blue on cooling. It dissolves in water with a green colour, which on addition of a little nitric acid turns red. Other characteristic reactions for the manganese salts are the following. Potash and soda precipitate the white hydroxide, which soon becomes brown on exposure to air. Ammonia in the presence of ammonium chloride produces no immediate precipitate, but the solution rapidly absorbs oxygen from the air, brown manganic hydroxide being deposited. When a manganese compound is fused in a borax bead an amethyst-coloured bead is obtained in the outer flame, and this in the inner flame becomes

[1] Hartley and Ramage, *Journ. Chem. Soc.* 1893, **1**, 129.

colourless. The non-luminous gas-flame is coloured green by manganese chloride, and this exhibits a spectrum in which the lines in the green and yellow are the following:[1]

$$\alpha = 5587 \qquad \beta = 5392 \qquad \gamma = 5195$$

The spark-spectrum of manganese contains a large number of bright lines, of which the following are the most important (Lecoq de Boisbaudran):

Orange { 6022, 6017, 6014 } Green { 4824, 4784 } Blue { 4766, 4762, 4754 } Indigo { 4235, 4228 }

The absorption-spectrum of permanganic acid and its potassium salt exhibits in very dilute solution five distinct bands; a more concentrated solution gives continuous absorption in the yellow and green; and this is also observed in certain solutions of manganic salts. The latter, however, do not show the bands on dilution.

In order to determine manganese quantitatively it may be precipitated as the carbonate or phosphate. Frequently, however, it is thrown down as the peroxide by treating the solution with bromine water and ammonia. This is then converted by ignition into the red oxide, Mn_3O_4, in which condition the manganese is weighed. The sulphide on heating in the air is also converted into the same oxide. This oxide is however very liable to reduction or oxidation, and the amount of available oxygen in it should always be ascertained volumetrically.

Manganese always occurs in nature together with iron. In order to determine this quantitatively, the solution is heated with sal-ammoniac, neutralised with the requisite quantity of ammonia, and the iron precipitated with ammonium acetate. The manganese can then be determined in the filtrate in the above way.

Manganese may be estimated volumetrically by titration with potassium permanganate (p. 920) or by conversion into permanganate, which is then estimated by titration with standard oxalic acid, hydrogen peroxide, or some other reducing agent. When small quantities are concerned this is best done by boiling the manganese salt with concentrated nitric acid, solid lead peroxide, and a little dilute sulphuric acid, and filtering the resulting

[1] Hoppe-Seyler, *J. Chem.*, 1870, **110**, 303.

liquid through asbestos, or by digesting the salt with nitric acid and sodium bismuthate.

Evaluation of Manganese Ores.—The most accurate and convenient methods for the assay of manganese ores are those of Bunsen,[1] and of Fresenius and Will.[2] By the former method the quantity of chlorine which is evolved on treatment with hydrochloric acid is directly determined:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The free chlorine is collected in a solution of potassium iodide, and the liberated iodine estimated with a dilute solution of sulphurous acid or sodium thiosulphate.

Fresenius and Will's gravimetric method depends upon the fact that when manganese dioxide and oxalic acid are brought together in presence of sulphuric acid, the following decomposition occurs:

$$MnO_2 + C_2O_2(OH)_2 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

Or 87·34 parts of carbon dioxide correspond to 86·36 parts of manganese dioxide. This is carried out in a weighed apparatus provided with a drying tube, the loss of weight being ascertained.

The *atomic weight* of manganese has been determined by several chemists. Berzelius[3] found that 4·20775 parts of manganous chloride yielded 9·575 parts of silver chloride, whence the atomic weight 54·86 is calculated. Five similar determinations by Dumas[4] gave the number 54·58; and V. Hauer[5] by reducing manganous sulphate to sulphide in a current of hydrogen sulphide, obtained the number 54·50. Dewar and Scott, by estimating the percentage of silver in silver permanganate, obtained 54·64;[6] and Marignac, by converting pure MnO into $MnSO_4$, obtained 54·61.[7]

[1] *Journ. Chem. Soc.* 1856, **8**, 219.
[2] *Annalen*, 1843, **47**, 87.
[3] *Pogg. Ann.* 1828, **14**, 211.
[4] *Annalen*, 1860, **113**, 25.
[5] *Wien Acad. Ber.* 1857, **25**, 124.
[6] *Proc. Roy. Soc.* 1883, **35**, 44.
[7] *Fresenius Zeitsch.* 1884, **23**, 123.

GROUP VIII.

(*a*) Iron, Nickel, Cobalt.
(*b*) Ruthenium, Rhodium, Palladium.
(*c*) Osmium, Iridium, Platinum.

522 The metals placed by Mendeléeff in the eighth vertical group form a very remarkable feature of his arrangement of the elements. They occur in three sub-groups, each containing three metals, forming the termination of the even horizontal series, Nos. 4, 6, and 10, each group being the connecting link between the elements of the even series which precede it and those of the odd series which follow. The three metals which make up each horizontal sub-group resemble one another very closely, and differ much less in atomic weight, atomic volume, and general physical properties than is usual in the successive elements of a horizontal series, as may readily be seen by a reference to Lothar Meyer's diagram (p. 55).

This remarkable similarity is borne out by the chemical behaviour of these elements, the various platinum metals, for example, being so similar that their separation from each other is a matter of the greatest difficulty, and this is also true of nickel and cobalt.

At the same time a certain degree of similarity can be traced between those metals which are in the same vertical column, more particularly in sub-groups *b* and *c*. Thus ruthenium and osmium, rhodium and iridium, palladium and platinum agree very closely in many of their most characteristic properties, such, for example, as the formation of a tetroxide, which is peculiar to ruthenium and osmium, &c.

From the analogy of the preceding groups, it would be expected that the characteristic oxide of the metals of this group would have the formula MO_4 or M_2O_8. Actually, however, only ruthenium and osmium form such an oxide, whilst all the metals of the group form lower oxides, many of which correspond to series of stable salts.

A very characteristic property of the metals of this group is their tendency to form complex radicals with other elements or groups, which then act as basic or acidic radicals, and thus give rise to extended series of compounds. These substances, as a

rule, differ entirely in properties from the ordinary salts of the metal, this being due to the fact that each radical has its own characteristic properties, and those of the metal only appear when the radical has been broken up. Some of the most important of these complex derivatives are the double cyanides, such as the ferrocyanides and their analogues, the chloroplatinic acids, the ammoniacal derivatives of cobalt and of the platinum metals, the double nitrites, sulphites, &c. This tendency is to some extent shared by chromium, manganese, and copper, and other metals which either immediately precede or follow the metals of Group VIII. in the periodic system.

SUB-GROUP (*a*). THE IRON GROUP.

Iron, Nickel, Cobalt.

523 These three metals are all magnetic, melt at a high temperature, are oxidised when strongly heated in air or oxygen, and decompose steam at a red heat. They all form basic oxides of the formula $M''O$, and a corresponding series of coloured salts in which the metal is divalent. The sesquioxides $M_2'''O_3$ also act as basic oxides, but the corresponding salts of nickel and cobalt are so unstable that they speedily decompose with formation of salts corresponding to the lower oxide. Those of iron, on the other hand, are much more stable, and are formed from those of the lower oxide on exposure to the air. These metals, moreover, all yield oxides of the formula M_3O_4, to which no stable salts correspond, and which are probably to be considered as being themselves salts of the formula $M''M_2'''O_4$. Cobalt, in addition to these, forms an unstable acidic dioxide, whilst derivatives of the corresponding nickel oxide are also known, but no such derivatives of iron have been prepared, although the corresponding sulphide exists as iron pyrites. Iron, however, forms a series of compounds known as the ferrates, which are derived from a hypothetical acidic trioxide, FeO_3, to which no analogue is known among the compounds of nickel and cobalt.

Nickel and iron both unite with carbon monoxide to form volatile liquids, whereas cobalt does not appear to form such a compound.

Nickel has much less tendency to form complex radicals than

cobalt or iron, the most important of these derivatives formed by the last two being the cobaltammines and the cyanogen compounds of iron.

IRON (FERRUM). Fe = 55·6.

524 Iron is the most important of all the metals. It seldom occurs in the metallic state in nature; the ores of iron are, however, found widely distributed, and usually in a state of purity; and the reduction of metallic iron may well be considered as one of the simplest of metallurgical operations, requiring far less knowledge and skill than is needed for the preparation of bronze. In spite of these facts it is usually supposed that the iron age followed those of copper and bronze, although in many cases the art of working in iron became known at a very early period. It is, however, to be remembered that metallic iron is rapidly destroyed by rusting, at any rate in damp situations, and this may to some extent account for the comparatively rare occurrence of very early iron implements.

It appears probable that iron was first obtained from its ores in India, and it is certain that both the Assyrians and the Egyptians employed iron implements many centuries before our era. In the Pentateuch the metal iron is mentioned, as well as the furnaces in which it was prepared; the Hebrew name for iron, Barzél, is derived from the root Bazal, which signifies to be hard, whilst the derivation of the Greek word σίδηρος which occurs in Homer is unknown. The Greeks obtained their iron from the Chalybes, a nation dwelling on the south coast of the Black Sea, from whom the Asiatic nations also obtained iron. The Romans, on the other hand, not only procured their iron from this district, but also from Spain, Elba, and Noricum. The Elban iron mines, which are to this day renowned for their fine specular iron, were worked by the Etruscans, and the method which was employed by them for the extraction of the iron is identical in principle with that still in vogue in the Pyrenees.

The word iron, which is identical with the Scandinavian "iarn" (instead of "isarn"), and with the German "Eisen" (adjective, "eisern"), appears to be connected with the Sanscrit "ayas" (Latin "aes"), and this, according to Grimm, is an indication that bronze was in use among the Germans at a much

earlier date than iron. The alchemists connected iron with Mars, the god of war, and gave to it the sign ♂.

Native iron occurs, according to Andrews,[1] in small spiculæ distributed throughout the basalt of the Giant's Causeway, as well as in the old lavas of the Auvergne. The occurrence of terrestrial iron in large lumps has also frequently been observed: these masses have, however, been formed in the firing of coal-pits when the burning mass has come in contact with ores of iron, and the product of the action is termed natural steel.

The native metal occurs more frequently in the form of *meteoric iron*. The meteorites falling in larger or smaller masses from extra-terrestrial sources may be divided into two groups, "Earthy meteorites," which chiefly consist of silicates, and "Meteoric irons," which consist of iron together with a larger or smaller quantity of nickel, the presence of this latter metal being characteristic of meteoric masses. Meteoric iron likewise usually contains small quantities of cobalt and other metals, as well as graphite, ferrous sulphide and schreibersite, Ni_2Fe_4P, this last compound being one which does not exist in any terrestrial mineral. When the surface of a meteoric iron is planed and polished, and then treated with dilute nitric acid, peculiar configurations make their appearance which were first noticed by Widmanstätten in the year 1808. These consist of rhombic folia or crystalline markings (shown in Fig. 163) which have a metallic lustre; the spaces enclosed by these markings are somewhat raised, so that a surface of meteoric iron thus treated may be used as a plate from which an engraving can be obtained. Some meteoric irons do not exhibit these figures, parallel striæ making their appearance when the metal is subjected to a similar treatment. Meteoric iron frequently occurs in considerable masses; thus, for instance, that which was discovered by Pallas in Siberia originally weighed 800 kilos. [Analysis (*a*)], whilst that found in Bahia weighed nearly 7,000 kilos.; a still larger mass occurs at Chaco-Gualamba in Peru, which is said to weigh 16,000 kilos., and similar large masses have been found in other localities both in North and South America, as well as in Africa. The largest known masses are those found at Ovifak on the island of Disko, off Greenland,

Fig. 163.

[1] Andrews, *Brit. Assoc. Report*, 1852.

where fifteen blocks of meteoric iron occur, the weight of the two largest being, according to Nordenskjöld,[1] 21,000 and 8,000 kilos [see Analysis (*b*)].

The following table gives the composition of several meteoric irons :—

	(*a*)	(*b*)	(*c*)	(*d*)
Locality . . .	Siberia.	Ovifak.	Brazil.	Tennessee.
Analyst . . .	Berzelius.	Nordenskjöld.	Damover.	J. L. Smith.
Iron . . .	88·04	84·49	63·69	91·15
Nickel . .	10·73	2·48	33·97	8·01
Cobalt . .	0·46	0·07	1·48	0·72
Copper . .	0·07	0·27	0·05	0·06
Manganese	0·13	—	—	—
Carbon . .	0·04	10·62	0·02	—
Sulphur .	trace	1·52	0·02	—
Phosphorus	—	0·20	0·05	—
Chlorine .	—	0·72	—	—
Silicate . .	0·53	0·09	—	—
	100·00	100·46	99·28	99·94

Finely divided meteoric iron is constantly falling from extra-terrestrial space on to the earth : the occurrence of this meteoric dust has been observed in Sweden and in the snow-fields of Northern Siberia, the snow enclosing black magnetic particles which contain cobalt as well as iron. More recently similar particles of meteoric dust, consisting of metallic iron, have been found by Murray, of the *Challenger* expedition, at great depths in mid-ocean. It is only under conditions such as the above that it is possible to detect this fine meteoric dust in consequence of the enormous accumulation elsewhere of terrestrial dust.

525 Iron is usually found in combination either with oxygen or sulphur. Of the large number of minerals which contain iron only those will now be mentioned which occur most commonly and in largest quantity; the ores will be specially described hereafter. The most important oxygen compounds of iron are red hæmatite, or specular iron, Fe_2O_3; brown hæmatite, $Fe_4O_3(OH)_6$; magnetic iron, Fe_3O_4; spathic iron, $FeCO_3$, which latter also contains other isomorphous carbonates. Again, iron pyrites, FeS_2, occurs largely, whilst magnetic pyrites, Fe_7S_8, is less common; ferrous sulphide also forms an important

[1] *Pogg. Ann.* 1874, **151**, 154.

constituent of copper pyrites, $CuFeS_2$, arsenical pyrites, $Fe(AsS)_2$, and other minerals. Silicates of iron are found in most geological formations, and from these iron oxide finds its way into the soil, in which it is usually present in considerable quantity, imparting to it a reddish or brown colour. This fact was known to Pliny, who mentions that the presence of iron may be recognised by the colour of the soil. Iron compounds are contained in solution in spring- and river-waters, as well as in the water of the ocean, and it is from one or other of these sources that plants obtain the iron which forms a necessary constituent of their chlorophyll.

In 1702 N. Lemery proved that the ashes of plants contained iron: this observation was confirmed by the experiments of Geoffroy in 1705, who, however, assumed that the iron was not originally contained in the plants, but that it was produced when they were burned. Other celebrated chemists, such as Becher, held the view that the iron which made its appearance when certain substances were subjected to chemical treatment was not contained in them but was independently produced. This erroneous opinion was first disproved by Lemery.

Iron likewise forms a necessary constituent of the animal body; thus for instance, hæmoglobin, the red colouring-matter of the blood, contains 0·24 per cent. of iron. Iron preparations have also long been employed as a medicine, especially in chlorosis, general debility, and loss of blood; and it has now been ascertained that after the use of iron the number of red corpuscles is increased, and the amount of hæmoglobin which they contain becomes larger. At the same time the nutritive processes of the body are accelerated, as is evidenced by a rise in temperature, and an increase in the quantity of urea secreted. The presence of iron in the blood was first shown by Menghini of Bologna in 1747.

The existence of iron in large quantities in meteoric masses indicates a wide cosmical distribution of this element, and this conclusion has been confirmed by Spectrum Analysis, which indicates to us the presence of iron in the sun and many fixed stars.

526 *Preparation of pure Iron.*—Iron is usually produced from its oxides by means of charcoal, and is thus obtained on the large scale; thus prepared, however, iron is not pure, but contains more or less carbon. The purest commercial form of iron is wrought iron, especially the finest kinds of piano-wire: this

contains about 0·3 per cent. of foreign impurities chiefly consisting of carbon. In order to obtain chemically pure iron the oxide, or oxalate, may be heated in a current of hydrogen at the lowest possible temperature; the metal is obtained by this process as a black powder which oxidises and becomes incandescent in the air, but if the reduction be carried on at a higher temperature the powdered iron is not pyrophoric.

Pure iron may be obtained by the reduction of ferrous chloride, $FeCl_2$, in hydrogen, when the metal is deposited in microscopic quadratic octohedra or cubes (Péligot).[1] It may also be prepared by electrolysis. For this purpose a solution of ferrous sulphate is prepared and then mixed with sal-ammoniac and magnesium sulphate; on electrolysis the iron is deposited in bright grey plates. Electrolytic iron has the power of occluding certain gases, especially hydrogen; on heating the metal in a vacuum these gases are given off, and the metal which remains has a white colour resembling platinum. In order to obtain pure iron as a coherent metallic mass a mixture of equal parts of pure Glauber's salt and iron sulphate is ignited in a platinum crucible until no further evolution of sulphur dioxide occurs; on washing the mass with water a crystalline precipitate of ferric oxide remains behind: this is next placed in a platinum crucible and reduced in hydrogen. The porous mass of reduced iron is then pressed into a lime crucible and melted by means of the oxyhydrogen blowpipe.[2] It is doubtful whether the fused metal thus prepared is quite pure.

Good wrought iron when melted in this way also yields a regulus of pure metal, especially if towards the end of the operation the current of oxygen be increased, when the impurities are oxidised and absorbed by the porous mass of the crucible.[3]

527 *Properties.*—Pure iron has a specific gravity of 7·84, and a specific heat of 0·1113 at 50°;[4] it possesses an almost silver-white lustre, and takes a high polish; it is the most tenacious of all the ductile metals except cobalt and nickel; it becomes soft at a red-heat, whilst at a white-heat it can be readily welded, but if heated above the welding-point it is brittle under the hammer. Pure iron is more difficultly fusible than wrought iron, but it can be volatilised when heated in the

[1] *Compt. rend.* 1844, **19**, 670.
[2] Mattheissen and S. P. Szczepanowski, *Chem. News*, 1869, **20**, 101.
[3] Troost, *Bull. Soc. Chem.* 1868 [2], **9**, 250.
[4] Naccarri, *Journ. Chem. Soc.* 1888, ii, 1236.

electric furnace. Even when iron is burned in oxygen a small quantity of the metal is vaporised and is seen to burn. Iron is attracted by the magnet and may also be rendered magnetic, but it loses this latter property after a short time, whilst carbonised iron or steel retains this polar condition at the ordinary temperature, losing it however at a red-heat. Iron does not undergo any alteration in dry oxygen or in pure air at the ordinary temperature, nor does it decompose water free from air even when warmed. In moist air, at the ordinary temperature, it becomes coated with ferric hydroxide, or iron rust, this oxidation being greatly assisted by the presence of carbon dioxide or small quantities of acid vapours. In contact with air and water, and with certain acids and salts, especially ammoniacal salts, this oxidation or rusting is promoted, whilst the liability to rust is diminished in the presence of alkalis. The formation of rust takes place to begin with but slowly, whereas if a very thin superficial coating of oxide has been formed, the process goes on quickly. In order to diminish the liability to rust, iron articles are painted with varnishes, or oil-colours, or the surfaces are covered with oil, fat, or graphite. A coating of black magnetic oxide of iron, Fe_3O_4, serves, however, as the best protection against the rusting of iron. For the purpose of coating objects of iron with this oxide, Becquerel places the iron as the positive electrode in a solution of sulphate of iron and sal-ammoniac, whilst the process patented by Barff consists in exposing the iron to the action of superheated steam at a temperature of about 650°, when a film of hard magnetic oxide is formed on the surface, and this does not undergo any further change, and is said effectually to protect the metal. In contact with metallic zinc iron becomes electro-negative, and is thus to a certain extent protected from rusting. Iron articles are often covered with a coating of zinc (galvanised iron), tin (tin plate), or nickel, to protect them from rust.

Iron combines readily with the elements of the chlorine group, and when strongly heated burns in oxygen, forming the magnetic oxide, and at a red-heat decomposes steam with formation of the same oxide; it also burns at a red-heat in sulphur vapour, and combines with carbon when brought in contact with it at a high temperature, and for this reason all the iron obtained on the large scale contains carbon in combination; the larger the quantity of this element it takes up, the more readily fusible is the iron (p. 943).

Iron dissolves in most dilute acids with evolution of hydrogen. Dilute nitric acid dissolves it in the cold without the evolution of any gas and with the formation of ferrous nitrate, $Fe(NO_3)_2$, and ammonium nitrate; when heated, or when a stronger acid is employed, oxides of nitrogen are evolved and ferric nitrate, $Fe(NO_3)_3$, is formed.

Passive Iron.—Under certain circumstances iron is apparently not acted upon at all by nitric acid, nor does it, when in this condition, precipitate copper when brought into solutions of this metal. Iron in this state is termed passive, and this condition is brought about by dipping the metal into concentrated nitric acid and then washing it (Keir).[1] Other substances, such as chloric, bromic, iodic, and chromic acids, and even hydrogen dioxide, act upon iron in a similar way. According to Faraday and Beetz the passive condition of iron depends upon the formation of a very thin film of oxide, and this conclusion is confirmed by the fact that iron wire may also be made passive by a moderate ignition.

According to Gautier and Charpy, passive iron is slowly attacked by nitric acid, since the acid, after having been in contact with the metal for some time, gives a precipitate of ferric hydroxide with aqueous potash.[2] Magnetised iron appears to be rather less passive than ordinary iron.[3]

Finely Divided or Reduced Iron (ferrum redactum) has long been used in medicine. *Spongy iron* is now prepared on the large scale by the reduction of burnt pyrites or blue-billy and other ores of iron, and used as a means of filtering and purifying water for domestic use (Bischof).

528 *Iron amalgam* does not form readily, but on acting with a one per cent. sodium amalgam upon a solution of ferrous sulphate, a semi-solid mass is obtained which, when in small globules, is attracted by the magnet. On distilling this amalgam, metallic iron remains in a fine state of division (Böttger). The same amalgam can be formed by rubbing powdered iron with mercuric chloride and water. If an iron wire be attached to the copper-pole of a Daniell's element, and dipped into a solution of ferrous sulphate, whilst another iron wire from the zinc-pole touches a drop of mercury lying in the solution, amalgams of varying composition are obtained according to the intensity of the current. Those containing

[1] *Phil. Trans.* 1790, 379. [2] *Compt. rend.* 1891, **112**, 1451.
[3] Andrews, *Proc Roy. Soc.* 1891, **48**, 116, **49**, 120, 481.

only small quantities of iron are liquid; those in which more iron is present are soft and crystalline. One containing 103·2 of iron to 100 of mercury forms a hard black mass obtained by pressing the liquid amalgam under a pressure of 50 tons to the square inch.[1]

METALLURGY OF IRON.[2]

529 Several mythical stories point to the fact that in very early times meteoric iron, which falling from the heavens was considered as a gift of the gods to man, was employed in the manufacture of iron weapons. This indeed appears to be a practice still employed by certain uncultured tribes; the Esquimaux, as we hear from Ross, employ meteoric iron for the manufacture of their implements, and Kumbary[3] relates that the chiefs in the Wadai country, in Central Africa, possess many weapons which have been worked up from meteoric masses. But meteoric iron occurs so sparingly upon the earth's surface and is in fact so unsuited to the manufacture of tough forgings, that at a comparatively early period in the history of civilisation men set about the smelting of iron from its ores.

The enormous deposits of ancient slag and furnace-cinder which are found spread over large areas in various districts of India point to the fact that the iron industry existed in that country at very early times, and even to the present day the manufacture of iron is carried on in India in the most primitive manner. It is also clear that the ancient Assyrians and Egyptians were well acquainted with the uses of iron, and the remains of their iron works have been found near Sinai. But, independently of these sources, a knowledge of the methods of working iron ores also appears to have been gained by the tribes living in the North of Europe, whilst the inhabitants of the Western Hemisphere were not acquainted with these processes. Little is known respecting the method employed by the ancients in the manufacture of iron; the slight information which we possess has been collected together by Agricola in his work, "De Veteribus et Novis Metallis." The apparatus employed

[1] Joule, *Journ. Chem. Soc.* 1863, 378.

[2] Further information on this subject may be obtained from the metallurgical works of Percy, Turner, and Howe.

[3] *Compt. rend.* 1870, **70**, 649.

was evidently of a primitive kind, and consisted of a small hearth or furnace to which was attached a bellows or blowing arrangement driven by hand, similar indeed to that which is now in use among the hill-tribes in India and in Central Africa. Malleable iron and steel are both produced by igniting the iron ore with charcoal, the metal being obtained in the form of a porous lump or "bloom," which was pressed or hammered into a coherent metallic mass.

The dexterity exhibited by the Hindoos in the manufacture of wrought iron may be estimated from the fact of the existence in the Mosque of the Kutub near Delhi of a wrought-iron pillar no less than 60 feet in length.[1] This pillar stands about 30 feet out of the ground, and has an ornamental cap bearing an inscription in Sanskrit belonging to the fourth century. It is not an easy operation at the present day to forge such a mass with our largest rolls and steam-hammers; how this could be effected by the rude hand-labour of the Hindoos we are at a loss to understand.

Cast Iron, Wrought or Malleable Iron, and Steel.

530 The iron which is obtained from its ores by metallurgical processes is never pure, but invariably contains other constituents, which greatly affect the properties of the metal, and determine its value for various purposes. The most important of these additional constituents are carbon, silicon, phosphorus, sulphur, and manganese, and it is found that comparatively small variations in the amounts of these substances which are present exert an enormous influence on the properties of the metal.

Three main varieties of commercial iron are usually distinguished:

(1) *Cast iron* contains 1·5–4 per cent. of carbon, besides varying quantities of the other elements mentioned above. This variety fuses readily, and when cold is brittle and cannot be worked under the hammer.

(2) *Wrought* or *malleable iron* contains less carbon than the foregoing, and fuses less readily, but is malleable when cold and

[1] A cast of this pillar is to be seen in the Architectural Court of the South Kensington Museum, and a drawing of the same is found in St. John Day's *Prehistoric Use of Iron and Steel*, p. 144.

can therefore be worked under the hammer, and can be welded at a red-heat. The characteristic feature of malleable iron is that it is produced in a pasty state without having been melted, and consequently contains particles of slag, which cannot be completely removed from the unfused metal.

(3) *Steel* comprises all malleable alloys of carbon and iron which have at any time been actually melted. It does not contain slag particles, but otherwise does not necessarily differ in composition from malleable iron. Steel possesses the valuable property of becoming hard when it is suddenly cooled from a high temperature, the intensity of this effect depending upon the amount of carbon which it contains.

The general process of iron smelting consists essentially in the removal of the oxygen from the ores, and this is invariably carried out in practice by the action of carbon at a high temperature. In addition to the oxygen, the extraneous matter contained in the ore, such as silica, alumina, sulphur, phosphates, &c., must also be removed, and the resulting iron must be exposed to such conditions that it acquires the composition which will fit it for the special purpose to which it is to be applied.

Ores of Iron.

531 The term iron ore includes all those minerals which contain iron not only in a sufficient quantity, but also in a condition which enables them to be employed for the economic production of the metal. Thus, for example, iron pyrites, FeS_2, although it occurs in very large quantities and contains a high percentage of iron, cannot properly be described as an iron ore, inasmuch as it is difficult to completely remove the sulphur, a small proportion of which renders the metal unfit for use. In like manner arsenical pyrites, although it also contains a large quantity of iron, is unfit for the production of the metal; and the same may be said of many other minerals which contain large quantities of iron.

The various ores of iron are composed of, or contain, the oxides of iron in more or less pure condition, and the value of an iron ore is influenced rather by the nature of the impurities which it contains than by its percentage of iron.

The ores of iron occur almost in every geological formation; thus magnetic iron ore is found in the older rocks, as in the

Laurentian beds of North America, and the old slates and gneisses of Sweden, whilst red hæmatite occurs in beds or pockets in the Carboniferous limestone of Cumberland and North Lancashire, and spathic or clay iron-stone in the coal-measures. Again, the Oolitic rocks furnish large deposits of brown hæmatite, and the Elba ore is probably a Tertiary deposit. Still more recent formations of iron ore are seen in the bog ore of Germany and the North of Ireland, whilst "lake ores" are being formed in Scandinavia at the present day.

Magnetic Iron Ore, Magnetite, Loadstone, Fe_3O_4.—This ore, in the pure state, constitutes the richest and most valuable ore of iron, containing 72·4 per cent. of the metal. It occurs in the crystalline and massive state as well as in the form of sand, and is found in large deposits, especially in volcanic rocks, as well as in granite, gneiss, and mica-schist. This ore of iron is difficultly reducible, but it yields excellent iron and steel. The most important localities of magnetite are Arendal, Dannemora, and other places in Norway, Sweden, and Lapland; the island of Elba; the Ural Mountains; and several localities in the United States, especially near Lake Superior. In England magnetic oxide of iron occurs in Rosedale in Yorkshire, at Dartmoor, at Brent in South Devon, and at Treskerby in Cornwall; but it cannot be said to be an important English ore. In Germany it is found in large quantities at Schmiedeberg, in Silesia, and a few other localities.

The ore usually contains about 10 per cent. of insoluble matter, and is remarkably free from sulphur and phosphorus, as will be seen from the analysis on p. 948. The relation between the amounts of the two oxides present varies considerably in different ores, according as the monoxide has been more or less completely oxidised to the sesquioxide.

Franklinite, $(FeMn)_2O_3(FeZn)O$, occurs in New Jersey, and is first worked for zinc, the residue being used as an iron ore.

Red Hæmatite, or *Specular Iron Ore,* Fe_2O_3.—This substance occurs crystalline as specular iron ore, and also in a massive state having a columnar, granular, or botryoidal form, as well as in the earthy condition. This ore, being free from impurities, yields a cast-iron which is especially well adapted for the manufacture of malleable iron and steel. Hæmatite occurs in veins as well as in beds and pockets. One of its most remarkable localities is the island of Elba, where it occurs finely crystallised between talcous schist and crystalline

limestone. The Elban mines were worked by the Etruscans and are still productive. A fine hæmatite occurs in the Huronian rocks on the southern shore of Lake Superior, whilst at Iron Mountain, near St. Louis, Missouri, enormous masses of this ore of iron are found. On the continent of Europe hæmatite occurs in Belgium, and deposits of this ore are also found in the Devonian formation on the Lahn in Westphalia. The chief deposits of hæmatite in England are those near Ulverston in Lancashire, and on the coast of Cumberland near Whitehaven; the ore here occurs in beds or pockets in the Carboniferous limestone, sometimes existing as hard botryoidal masses exhibiting crystalline structure, and sometimes in a soft or compact amorphous condition.

The specular iron from Elba occurring in large crystals consists, according to Rammelsberg, of iron sesquioxide together with 0·3 per cent. of titanium dioxide, sometimes as much as 0·8 of iron monoxide and 0·4 per cent. of magnesia. American hæmatites are also frequently extremely pure; thus Jordan found that an ore from Michigan contained the following impurities: 0·09 lime, 0·11 magnesia, 0·28 insoluble residue. The ore as employed for the production of iron is always more or less mixed with "gangue," as is shown from the analysis on p. 948.

Brown Hæmatite, or *Limonite*, $Fe_2O_3+2Fe(OH)_3=2Fe_2O_3+3H_2O$.—This substance occurs crystallised in rhombic prisms, but is more frequently found either in a fibrous foliated and scaly condition, or as a dark brown reniform mass and commonly known as Brown and Yellow Hæmatite. In the massive state this ore occurs in large quantity and, as it can be readily worked, it has been long employed as a source of iron (for analysis see table on p. 948). It is found in the Carboniferous limestone as well as in the older rocks, in the Forest of Dean, and Llantrissant in Glamorganshire in the lower coal-measure sandstones. At Bilbao in Spain it occurs largely in the Carboniferous limestone, whilst the newer and earthy brown hæmatite is found in the oolite and green-sand in Northamptonshire and Lincolnshire. It is likewise largely worked in Germany and France, being the ore from which the greater part of the iron made in these countries is derived. The bog ores which are worked in the plain of North Germany and Canada and in other places, as well as the peculiar iron ore of the North of Ireland and the Swedish lake ore, belong to this class, and are of the most recent geological formation.

Spathic Iron Ore, or *Siderite.*—Spathic iron ore consists of ferrous carbonate, $FeCO_3$, invariably mixed with the isomorphous carbonates of manganese, magnesium and calcium. It possesses a yellowish-brown colour, and occurs often in globular or botryoidal forms having a silky fibrous structure. It is usually found in Devonian rocks, occurring in England at Brendon Hill in Somerset, at Exmoor and Weardale in Yorkshire. The most celebrated European locality is the Erzberg in Styria (see analysis, p. 948), where not less than 110,000 tons of ore are annually raised and used for the manufacture of the celebrated Styrian steel. Spathic iron ore also occurs in large quantity in Carinthia, at Stahlberg near Müsen, and at Siegen in Prussia.

Clay Iron-stone, or *Argillaceous Iron Ore* is a spathic iron containing clay or sand, and is chiefly found in nodules or bands interspersed throughout the clays and shales of the coal-measures. This ore is the most important English ore of iron, as fully one-half of the iron made in this country is reduced from clay iron-stone. The chief workable beds of British clay iron-stone occur in Yorkshire, Derbyshire, Staffordshire, Warwickshire, South Wales and Scotland.

The "black band" iron-stone is an important variety of this ore. It contains from 20 to 25 per cent. of coal, and is found in Lanarkshire, North Staffordshire, and South Wales. The Scotch beds were discovered by Mushet in 1800, but they were not worked until the year 1830. In 1855 the same ore was discovered in Westphalia, and it is also worked in Lower Silesia. The coal-measures of the Gard and of the Aveyron in France, and those in Pennsylvania and Maryland and other States, also contain large quantities of clay iron-stone. The same ore is found in strata in the Lias and also in the Oolitic and Tertiary rocks, the Cleveland iron ore belonging to this latter class. Analyses of some clay iron-stones are given on p. 948.

Calcination of the Ore.

532 Before treatment in the furnace many iron ores, especially the clay iron-stones and the brown hæmatites, are subjected to a process of calcination or roasting. The object of this is to expel water and carbonic acid, and also to render it more porous, and thus to facilitate the subsequent reduction of the

Analyses of the Chief Ores of Iron.

	Magnetic Iron Ore.	Red Hæmatite.	Brown Hæmatite		Spathic Iron Ore.	Clay Iron-stone.	
	Dannemora.	Ulverston.	Forest of Dean.	Spain.	Erzberg.	Lowmoor.	Cleveland.
Ferrous oxide	28·42	—	—	—	55·64	36·14	39·92
Ferric oxide	62·06	92·68	90·05	78·80	—	1·45	3·60
Manganous oxide	—	—	0·08	0·65	2·80	1·38	0·95
Alumina	—	2·80	trace	3·50	—	6·74	7·86
Lime	—	—	0·06	trace	0·92	2·70	7·44
Magnesia	1·44	—	0·20	trace	1·77	2·17	3·82
Alkalis	—	—	—	—	—	0·65	0·27
Carbonic acid	—	—	—	—	38·35	26·57	22·85
Sulphur trioxide	—	—	trace	—	—	—	—
Iron sulphide	0·07	—	—	—	—	0·10	0·11
Phosphoric oxide	—	—	0·09	0·07	—	0·34	1·86
Silica	} 7·60	} 4·52	} 1·07	} 5·55	—	17·37	7·12
Insoluble matter					—	—	—
Water	—	—	9·22	11·65	—	1·77	2·97
Organic matter	—	—	—	—	—	2·40	1·64
	99·59	100·00	100·77	100·22	99·48	99·78	100·41

metal. At the same time any sulphides which the ore may contain are oxidised and the sulphur expelled. The ordinary clay iron-stone is sometimes roasted in large open heaps, the ore being mixed with a sufficient quantity of coal to keep up a slow combustion. A preferable method is to calcine the ore in kilns or roasters, as in these the consumption of fuel is less and the product more uniform than in the ruder process of roasting in heaps.

The Manufacture of Cast-Iron.[1]

533 The application of the blast furnace to the manufacture of iron marks an era in the history of the iron industry, inasmuch as it was by its use that a continuous process of iron manufacture became possible. The discovery of a process by which fusible cast-iron can be prepared, appears to have been made, probably accidentally, about the end of the fifteenth century, in Germany, where the Stückofen had long been in use for manufacturing blooms. No description of the process is, however, to be found in the older writers upon metallurgy. Thus Agricola, writing in 1556, only mentions the older methods of iron making, although he appears to have been acquainted with cast-iron; at any rate the new method must have been at work in this country in 1543, for we find that in that year English cast-iron cannons were used. The great demand for cast-iron, which was of course all made with charcoal, soon leading to a destruction of our forests, it became necessary, in the first year of the reign of Elizabeth, to endeavour to replace charcoal by some other fuel. This was accomplished by the employment of coke instead of charcoal, a practice which was carried out in England by Dudley as early as the first half of the seventeenth century, but which afterwards fell into abeyance. It was subsequently revived by Abraham Darby at Colebrookdale, about the year 1735.

The blast-furnace consists of a shaft varying in height from 50 to 100 feet, the largest diameter being 14 to 22 feet. The essential parts of the furnace are, first, the hearth or crucible, and, second, a shaft or chimney formed of two truncated cones

[1] For further interesting information on this subject the reader is referred to Percy's admirable "Sketch of the History of Iron," *Iron and Steel*, p. 873, and to Turner's *Metallurgy of Iron and Steel*, vol. i. p. 1, *et seq.*

joined at their bases, the upper being termed the "body" and the lower one the "boshes." Fig. 164 shows the construction of such a furnace on the scale of 1 : 180.

The shaft, A Fig. 164, is 75 feet high, the diameter at the widest part (the belly or bosh) being 20 feet, whilst at the throat, B Fig. 164, it is 16 feet, and at the hearth, C Fig. 164, 11 feet. The shaft is constructed of an outer shell of wrought-iron or mild steel plates, supported by means of cast-iron columns, D Fig. 164, and is lined with fire-brick. In the lining of the boshes, which is exposed to the highest temperature, cooling boxes are inserted in many furnaces. These consist of narrow flat boxes made of gun-metal, which are built into the brickwork, and are cooled by a current of water, thus preventing the brickwork from becoming too hot. The wall of the hearth, which is also lined with fire-brick, is pierced by several openings; the tapping hole, E Fig. 164, by means of which the molten iron is periodically withdrawn; the slag-notch (not shown in the diagram), which is situated at a higher level, and through which the lighter slag is constantly allowed to flow away into trucks or ladles; and, finally, the openings by which the blast of air is introduced through the tuyères.

The throat of the furnace is closed by a contrivance known as the cup and cone arrangement, first introduced by G. Parry at the Ebbw Vale works in 1850. It consists of a cast-iron funnel, fixed at the mouth of the furnace, and closed by a cast-iron cone, suspended at one end of a counterpoised lever, or by means of a chain and wheel. When the cone is raised against the funnel (as shown in the figure) the throat of the furnace is closed, and the escape of gases into the air prevented; these then pass out of the furnace by the downcast, F Fig. 164, which is provided with a dust-catcher, G Fig. 164, and are then usually conveyed through the main to the stoves for heating the blast, to the boilers, or to any other point where the heat produced by their combustion can be made available. The charge is tipped from barrows on to the cone, and is introduced into the furnace by momentarily lowering the latter.

The blast of air is introduced near the bottom of the furnace through tuyère holes, perforating the walls of the hearth. The tuyères are made of wrought-iron, cast-iron, or bronze, and have a double casing through which water circulates to keep them cool; they vary in number from 2 to 12 according to the size of the furnace, are about 5 to 7 inches in diameter, and are

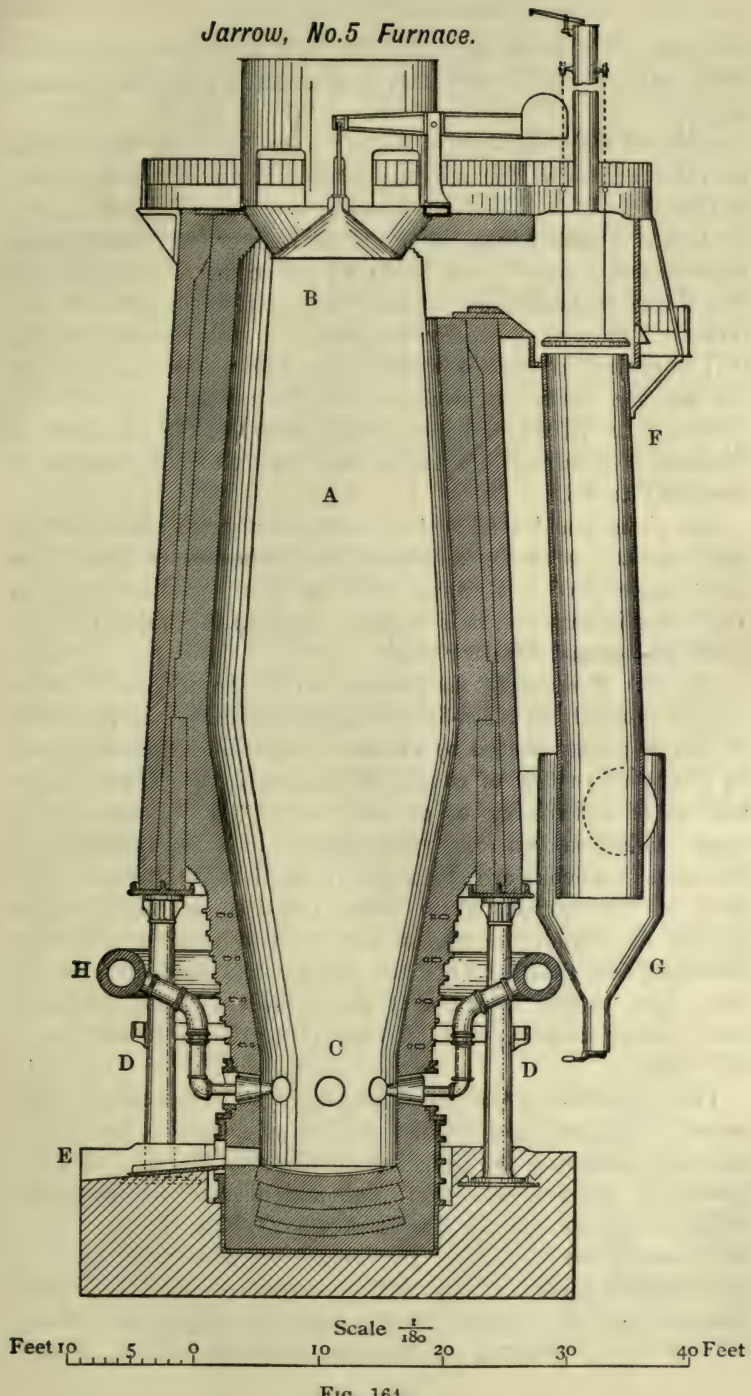

Jarrow, No.5 Furnace.
B
A
F
G
H
D
C
D
E
Scale 1/180
Feet 10 5 0 10 20 30 40 Feet

Fig. 164.

fed from an annular pipe, H Fig. 165, which surrounds the lower part of the furnace, and is connected with the blowing engine.

Hot and Cold Blast.—Up to the year 1828 air was blown into the furnace at the ordinary atmospheric temperature, but in that year J. B. Neilson[1] patented a process for heating the air before it passed into the forge or furnace, and this process, inasmuch as it saved from 15 to 45 per cent. of the fuel, and was also accompanied by an increased productive power of the furnace, was soon generally adopted, although the cold blast is still employed in certain works. For the purpose of heating the air, the waste gases from the furnace are burned in a Cowper's or Whitwell's stove, which acts on the principle of Siemens' regenerator, and raises the blast to a temperature of from 350° to 800°.

The air is thus introduced at a temperature of about 700° to 800°, and at a pressure of about 5 lbs. to the square inch. The total capacity of a furnace such as that described is about 14,150 cubic feet, and it is capable of producing about 1,000 to 1,300 tons of cast-iron per week.

534 *The Working of the Furnace.*—For the purpose of starting the newly-built blast-furnace it is necessary that the whole should be gently heated by means of a small fire, usually made by piling a quantity of rough dry timber in the hearth, on to the top of which charges of coke are placed. As soon as the shaft has become warm, regular charges of calcined iron-stone, limestone, and coke are added, until the furnace is filled. The blast is then turned on to about one-fifth of the quantity usually employed, the size of the tuyères being so gradually increased that it is not until the furnace has been in blow for from four to five weeks that the full-sized pipes are used, and several months generally elapse before the furnace is in full work.

The proportion of the materials employed, viz., iron-ore, limestone or lime, and fuel, termed the *charge* or *burden*, varies considerably according to the nature of the ore. If it be siliceous or clayey, the proportion of lime added must be increased; whilst if the ore contain lime instead of silica, the addition of silicates may be requisite. The object of these additions is to form fusible slags, so that the impurities of the ore may be removed and the furnace kept open and in proper working.

[1] Patent No. 5701, March 3rd, 1828.

The slag consists of silicate of lime and alumina, and it is extremely important that it be kept of the right basicity and fusibility. If the supply of lime and alumina is insufficient to combine with the silica present, oxide of iron passes into the slag thus causing waste, whilst if an excess of these bases be used the lining of the furnace is attacked. The fusibility of the slag moreover determines the temperature which can be reached and is therefore of great importance. The higher the temperature which is required for the reduction of the ore, the less fusible must be the slag. As soon as the proper proportions between the fuel, ore, and limestone have been ascertained, it is of the greatest importance that these proportions should be strictly adhered to, and for this purpose the charges are regularly weighed, and supplied in alternate piles at the top of the furnace, into which they are charged by lowering the cone, as already described.

On the average about one ton of coke and 8 to 12 cwt. of limestone are required for each ton of iron produced, about 100 tons of heated air being used in the operation. When the furnace is in regular blast, a constant stream of slag passes out from the slag-hole, the iron collecting in the lower part of the hearth, and being from time to time tapped by piercing a plug of sand and clay by which the tap-hole has been closed. Before tapping, the stove-man prepares moulds for holding the metal; these are formed in the sand as a series of parallel trenches, which are placed in communication with the tap-hole. The blast of air is then shut off, and the tap-hole opened by piercing the plug with a long bar of iron. The melted iron flows into the channels communicating with the moulds and assumes the form of semi-cylindrical bars or "pigs" united to one another by one of larger dimensions termed the "sow."

If, owing to some accident to the machinery, a blast-furnace is obliged to stand when hot, the operations may be suspended for several days if the throat and tuyère-holes be closed up with sand or clay. Should, however, serious damage have occurred, the furnace must be "blown out." This is accomplished by reducing the burden, and thus increasing the temperature for a time so as to remove any aggregations of solid matters which are fusible only at a high temperature. Finally, only fuel is charged, the contents of the furnace are allowed to burn out, and the last tapping is made at a point as low down in the hearth as possible. The life of a blast-furnace varies

considerably, lasting from two to twenty years, or even for a longer time, according to circumstances.

535 *The size and shape of blast furnaces* have been and continue to be very different. When charcoal is employed, as was formerly universally the case, and is still so in countries where wood is plentiful, the furnace is usually only from 20 to 30 feet in height. The charcoal iron which is thus manufactured in Sweden, Russia, and America is especially valuable for the preparation of fine iron wire, and of the best kinds of steel. Blast furnaces in which the fuel used is either coke, anthracite, or ordinary coal, are, on the other hand, of much larger dimensions, the exact height and capacity of the furnace being regulated by the nature and amount of iron which has to be produced, as well as (it may be added) by the ideas of the ironmaster.

In the year 1750 each English blast-furnace produced about 300 tons of pig-iron per annum, whereas a large-size modern furnace yields up to 62,400 tons in the same period. In the Cleveland district, where the blast-furnaces are unusually large, the average capacity of those built up to the year 1854 was about 7,000 cubic feet; whilst those built during the years 1870 and 1871 have an average capacity close upon 30,000 cubic feet, but in some cases the height rises to 105 feet and the capacity to 50,000 cubic feet. The production of a blast-furnace increases, of course, with its size, but not in a direct ratio; thus Sir Lowthian Bell has shown that an old furnace of 1853, having a capacity of 6,000 cubic feet, yielded one ton of iron per twenty-four hours for every 190 cubic feet of space; whilst in the high furnace built in 1870, 380 cubic feet of space are required to produce one ton of iron in the same time: hence the maximum limit of economic action may be passed by increased size. At the present day in England somewhat smaller furnaces are again being built.

The maximum production is at present gained in America, where larger furnaces, running up to about 90 to 100 feet in height, are employed, and the blast is fed at a higher pressure, averaging about 10 lbs. to the square inch. The furnace thus works more rapidly, producing as much as 100,000 to 150,000 tons per annum.

536 *Chemical Changes in the Furnace.*—A large number of investigations have been made on the subject of the changes which occur in the blast furnace, but in spite of these our knowledge of them is still far from complete. The fuel at the

hearth uniting with the oxygen of the blast, which is insufficient for its complete combustion, burns with formation of carbon monoxide. This gas coming into contact with the constantly descending charges of ore, reduces the ferric oxide to spongy metal, the change being accompanied by a slight evolution of heat:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 + 8{,}652 \text{ cal.}$$

The zone in which this reduction occurs most rapidly is near the top of the furnace, its exact position depending on the nature of the ore, and its temperature varies from 600–900°. When the ores are porous they are more easily permeated by the carbon monoxide, and the reduction takes place more quickly than when denser ores are employed. The reduction in this upper zone is never quite complete, because metallic iron is itself oxidised when heated either in carbon dioxide or in carbon monoxide, free carbon being deposited in the latter case. As the spongy iron, still containing a small amount of oxide, descends it arrives at the hotter parts of the furnace, the temperature of which reaches to 1000° in the belly or widest section. At this point the reduction of the metal is completed by the solid carbon present, some of which is supplied by the dissociation of carbon monoxide, which takes place at a high temperature, with formation of carbon dioxide and free carbon.[1] It has also been stated, although there is some doubt on the question, that the reduction is completed by the vapours of the cyanides of the alkali metals, the formation of which can be readily understood when we remember that the ores and limestone always contain alkalis, and which are moreover often actually obtained from the furnace. At this point, too, the spongy iron begins to take up carbon, but does not become saturated with it until a lower point has been reached, at which the temperature rises to about 1400°.

In this zone, which is the hottest part of the furnace, the materials, which were formerly in a pasty state, melt completely, running down into the hearth, where the lighter slag floats on the surface of the heavier iron, and thus protects it from the oxidising action of the blast. Other important changes in the composition of the iron occur as the metal passes down the furnace. In the first place, the spongy iron, in passing through the zone of reduction, takes up sulphur from the ores; and secondly,

[1] Cailletet, *Compt. Rend.* 1866, **62**, 891.

when the temperature reaches a higher point in the zone of carburisation, the phosphates contained in the ore are reduced, and the phosphorus is taken up by the iron. At a still higher temperature the fused iron in the presence of carbon reduces silicon from the silicates; and this, together with manganese, aluminium, and other metals, remains as a constituent of the cast-iron.

It will thus be seen that three main zones may be distinguished in the furnace. In the *first* and highest the greater part of the reduction occurs, whilst the partially reduced mass, in passing through the *second*, acquires the high temperature which is necessary for the reactions occurring in the *third* and last zone. These comprise the complete reduction of the ore, the carburisation and fusion of the metal, and its impregnation with silicon, phosphorus, &c. These various zones are of course not well defined, but pass gradually one into the other.

537 *Gases of the Blast-Furnace.*—The composition of the blast-furnace gases naturally varies in the different zones and under different conditions of burden. The relation of the carbon dioxide to carbon monoxide present in the blast-furnace gases is of great interest. The monoxide is reconverted during the reaction into the dioxide, and this either remains unaltered or is reconverted by the iron into the monoxide, according to the temperature which prevails in the upper part of the furnace. Carbon dioxide is also formed near the top of the furnace by the calcination of the limestone, and this is then partly reduced to the monoxide. The researches of Lowthian Bell and von Tunner have shown that the relation between the volumes of the escaping carbon dioxide and carbon monoxide, under otherwise similar conditions, serves as an excellent criterion of the economical working of the blast-furnace, and the limit of economical working is reached when from 40 to 60 volumes of carbon dioxide are present for 100 volumes of carbon monoxide. The furnace gases contain, in addition, nitrogen of the air, hydrogen derived from the reduction of aqueous vapour, as well as hydrocarbons, and frequently small traces of cyanogen or hydrocyanic acid.

Many analyses of the blast-furnace gases, collected at various heights above the tuyeres and under varying circumstances, have been made by several chemists. The following analyses give an idea of the varying nature of the composition of these gases:

Wood-Charcoal-Furnace at Veckerhagen, near Cassel. Height, 5·97 m. (Bunsen).

Depth in metres below the mouth—	0·86	2·59	4·32
Nitrogen	62·34	63·89	64·58
Carbon dioxide	8·77	3·60	5·97
Carbon monoxide	24·20	29·27	26·51
Marsh gas	3·36	1·07	1·88
Hydrogen	1·33	2·17	1·06
	100·00	100·00	100·00

Hot-blast Coke-Furnace at Seraing in Belgium. Height, 14·43 m. (Ebelmen).

Depth in metres below the mouth—	0·30	3·05	13·71
Nitrogen	57·06	61·67	54·63
Carbon dioxide	11·39	1·08	—
Carbon monoxide	28·61	35·20	45·05
Marsh gas	0·20	0·33	0·07
Hydrogen	2·74	1·72	0·25
	100·00	100·00	100·00

Cold-blast Coal-Furnace at Alfreton. Height, 11 m. (Bunsen and Playfair).

Depth in metres below the mouth—	1·52	5·18	10·36
Nitrogen	55·35	55·49	58·05
Carbon dioxide	7·77	12·43	—
Carbon monoxide	25·97	18·77	37·43
Marsh gas	3·75	4·31	—
Hydrogen	6·73	7·62	3·18
Olefiant gas	0·43	1·38	—
Cyanogen	—	—	1·34
	100·00	100·00	100·00

When coal is employed instead of coke in the blast-furnace the waste gases are passed through coolers and scrubbers to remove the valuable tar and ammonia which they contain, and are then passed on to the Cowper stoves, etc.

Amongst the products of the blast-furnace a variety of substances occur which choke or block up portions of the furnace.

Thus in smelting zinciferous iron-ores a compact incrustation of furnace-calamine, consisting chiefly of oxide of zinc, is found round the throat of the furnace, and no less than 100 tons of this compound, termed "gichtschwamm," are annually obtained from iron furnaces near Aix-la-Chapelle.

An interesting substance sometimes found in the blast-furnace is a cyano-nitride of titanium (p. 650); and, in addition to this, "kish," or graphite, as well as silicates, sulphides, and the oxides of other metals, occur as solid deposits in the furnace.

Varieties of Cast-Iron.

538 Fused cast-iron usually contains 1·5—4·5 per cent. of carbon, and when the iron is cooled this is either entirely retained in combination by the metal or is only partly retained, whilst the remainder separates out in the form of graphite, its behaviour being determined by the composition of the mass, the conditions of the process of manufacture and the mode of cooling. When the greater part of the carbon separates in the form of graphite, the resulting metal is known as *grey iron*, whilst when the whole or the greater part of it is retained in combination by the iron, the metal is known as *white iron*. Between these are several intermediate conditions classed together as *mottled iron*. All these names are derived from the appearance of a freshly fractured surface of the metal, the mottling characteristic of the last class being caused by the occurrence of spots of grey iron in a matrix of white.

When white iron is dissolved in hydrochloric or sulphuric acid various hydrocarbons are formed at the expense of the combined carbon which it contains, and these impart a peculiar and disagreeable odour to the hydrogen which is evolved. On the other hand when grey iron is treated with acids the graphite separates out in the form of black insoluble scales. This fact was known to Bergman, whilst Guyton de Morveau proved that cast-iron is formed when wrought-iron is ignited with diamond powder; and Karsten showed that cast-iron contains carbon both in the combined state and free in the form of graphite, this latter remaining behind when the iron is dissolved in an acid. The graphite can also be mechanically separated from the iron by sieving (Snelus).

Both the total amount of carbon present and the mode in

which it occurs depend very largely on the other substances contained in the crude iron, whilst these of course are determined by the conditions of the manufacture. Thus chromium and manganese favour the presence of a large amount of carbon, which is retained in combination when the iron cools, whereas silicon and aluminium diminish both the total amount of carbon present and the proportion of it which remains in the combined form. The way in which the metal is cooled also has a very important influence on the mode of occurrence of the carbon, slow cooling promoting the crystallisation of graphite and the consequent production of grey iron, whilst sudden cooling or chilling favours the production of the more homogeneous white iron. It is therefore possible, within certain limits, to obtain either grey or white iron from a given mass of the fused metal, simply by altering the conditions of cooling.

The following analyses of Cleveland pig[1] show the gradual variation in composition from grey, through mottled to white iron:

	Grey.	Mottled.	White.
Carbon. Graphitic.	3·20	1·84	—
„ Combined	trace	1·25	3·05
Silicon	3·50	1·01	0·67
Sulphur	0·05	0·32	0·40
Phosphorus . . .	1·67	1·57	1·60
Manganese . . .	0·68	0·62	0·42

The properties of cast-iron are also largely influenced by the amounts of silicon, phosphorus, sulphur, and manganese which are present.

White Iron is formed when the temperature of the furnace is not high enough for complete carburisation. It is very hard and brittle, and when fractured presents a very close grain. It melts at a lower temperature than grey iron, is less liquid, and after cooling is often found to be vesicular or honey-combed from the evolution of gas given off as the metal cools.

Grey Iron, on the other hand, is produced at a higher tempera-

[1] Quoted by Turner, *Iron and Steel*, **1**, 212.

ture, has an opened grained fracture and melts to a thinner liquid, being thus better adapted for fine castings than white iron. Both varieties of cast-iron expand somewhat (about 6 per cent.) on cooling at a temperature a little above their melting points, and then contract to the melting point on solidification.

Mottled Iron is intermediate in its properties between white and grey iron.

Spiegel or *Specular Iron* is a variety of white iron, in which manganese is present as an essential constituent, and contains a large proportion of carbon, varying from 3·5–6 per cent., practically all of which is in the combined form. It is extremely hard and brittle, and has a specific gravity of 7·6–7·7. When the alloy contains more than about 25 per cent. of manganese, it attains a granular structure and is termed *ferromanganese.* These two varieties are largely used in the manufacture of steel by the Bessemer process.

Irons containing large percentages of silicon and chromium are also manufactured in considerable quantities at present, and are employed for making special qualities of steel.

Manufacture of Wrought or Malleable Iron.

Malleable iron can be produced, either by the direct reduction of the ore under such circumstances that it cannot take up sufficient carbon, &c., to convert it into cast-iron, or indirectly from cast-iron by the removal of carbon and some of the other constituents.

(I.) The Direct Reduction of Malleable Iron from the Ores.

539 *Iron Furnaces.*—The simplest form of the iron furnace is that used at the present day on the west coast of India, as well as in the Deccan and Carnatic, and amongst the hill tribes. The low-caste Hindoos who work in iron, wander from place to place and build up their simple apparatus where they find fuel and ore; this latter consisting generally of magnetic oxide or brown hæmatite. The furnaces are built on the ground and constructed in the form of a round shaft or chimney, from 2 to 4 feet in height, having a diameter at the bottom of from

Analyses of Cast-Iron.

		Graphite.	Combined.		Sulphur.	Phosphorus.	Manganese	Chromium.	Iron.
			Carbon.	Silicon.					
White	Durham	—	4·10	0·23	0·03	0·07	2·37		
„	Alabama	0·10	2·92	0·95	0·30	0·64	0·10		
„	South Wales	—	2·40	0·80	0·70	1·50	0·20		
„	Staffordshire	0·20	2·00	0·71	0·19	0·47	0·50		
„	Schwechat	—	2·83	0·52	0·08	0·18	2·67		
Mottled	Ilsenburg	3·77	0·53	0·43	0·15	trace	1·43		
„	Cleveland	2·28	0·72	1·35	0·03	1·17	—		
„	Forest of Dean	2·37	1·31	0·40	0·06	0·07	0·11		
Grey	Forest of Dean	3·90	0·39	1·07	0·01	0·07	0·22		
„	Scotland	4·40	trace	2·68	0·08	0·10	—		
„	Staffordshire	3·30	0·40	1·88	0·02	0·71	0·40		
Spiegel	Dannemora	—	4·81	0·18	trace	0·12	1·99	—	92·90
Spiegel	Siegen	—	5·04	0·41	0·08	—	5·75	—	88·56
Ferromanganese	Prieger	—	7·15	0·87	0·02	0·07	72·75	—	19·14
Ferrosilicon	Darwen	1·20	0·23	14·00	0·08	0·08	1·95	—	
Ferrochrome	Darwen	—	10·05	0·40	—	—	0·42	63·10	25·38

10 to 15 inches, and at the top of from 6 to 12 inches. At the lower part there are two openings, one of which serves for the blast and the other for the exit of the slag which is formed by the silicates contained in the ore, as well as for the extraction of the bloom of iron. The bellows are usually made from a goat's-skin or a buffalo hide, furnished with bamboo tubes. As soon as the furnace is warmed with charcoal, layers of the broken ore and charcoal are built in the shaft, and after from 4 to 6 hours a porous bloom of iron is obtained, varying in weight from 5 to 30 lbs., and this is then worked under the hammer. Throughout Central India and in the north-east provinces the manufacture of iron is somewhat further advanced, the furnaces being larger and of a similar character to those which have been or are still in use in various parts of the world, as in Africa, Borneo, and certain parts of Europe. In many localities in England furnaces were erected on high ground, so as to take advantage of the prevailing wind to increase the draught. The word "hammer" which frequently occurs in place names in the south of England, usually marks the location of one of these old smelting works with its accompanying forge. Even to the present day the direct reduction of malleable iron from the ores is carried on in some European localities, especially in the Pyrenees and in certain districts of Spain, where a peculiar forge, termed the *Catalan forge*, is employed. The hearth of this furnace is about 3 feet long, 2 feet wide, and about 3 feet deep; at one side is an opening through which a *tuyère* is placed. The blast is supplied by the air carried down by a jet of falling water in a blowing machine termed a *trompe*. According to the size of the hearth the quantity of ore employed varies from 3 to 10 cwt., and this requires about its own weight, or rather more, of charcoal, and yields about 33 per cent. of iron. The ores employed are partly hæmatite and partly brown iron ore or spathic iron; the latter ores are previously roasted in order to expel water or carbon dioxide. At the beginning of the operation a weak blast is employed in order that the metal may be reduced by the carbon monoxide. The temperature is afterwards increased and pasty masses or blooms of metallic iron are obtained, which need only to be brought under the hammer to yield marketable bar iron. By a similar process the Elba specular iron has been worked up to within recent times in Corsica. In the United States, especially in districts where charcoal is plentiful, similar *bloomery forges* are still worked with a hot blast of

air. Some of these forges are capable of turning out a bloom of 300 pounds weight every three hours. The high bloomery furnace or "Stückofen" of the Germans is a blast furnace formerly in use in Carniola, and elsewhere, for the direct production of iron from the ore by reduction with charcoal. The process is, however, an expensive one owing to the large quantity of charcoal needed, and it has been superseded by other and cheaper methods.

(II.) Production of Malleable Iron from Cast-Iron.

540 The change which occurs in the conversion of cast into malleable iron consists essentially in the removal of a large proportion of the carbon, silicon, sulphur, phosphorus and manganese from the former, and is effected by oxidation in the presence of some substance which can unite and form a fusible slag with the silica and phosphoric oxide produced. As the removal of carbon, &c., proceeds, the melting point of the iron rises, so that at a certain stage the metal begins to solidify. It is then worked into a porous ball or bloom and hammered in order to forcibly squeeze out the slag which is contained in the pores.

In the older processes, the most important of which are the Styrian, Walloon and South Wales processes, the oxidation is carried out in open hearth furnaces, similar in general principle to that shown in Fig. 165. The cast-iron is simply melted on the hearth and exposed to a blast of air, by which it is partially oxidised. The oxides of iron thus produced react with the various constituents of the cast-iron and convert them into their oxides, which either escape in the gaseous form (carbon) or unite with another portion of the oxide of iron to form a slag (silicon, phosphorus), whilst the oxide of manganese unites with a portion of the silica. This process is specially adapted for white iron, and when grey iron is used, the first melting (*refining*) simply converts it into white iron without greatly altering the total amount of carbon present, most of the silicon being at the same time removed. A second similar operation (*fining*) is then necessary for the production of a satisfactory malleable iron.

The Puddling Process.—In 1784 Henry Cort introduced the puddling process, the essential feature of which is the use of a

reverberatory furnace instead of an open hearth furnace for the oxidation of the constituents of the cast-iron. In the older form of the process the oxidation was chiefly effected by the oxygen of the air, the reactions being precisely similar to those which occur in the open hearth process (p. 963). Like the latter it was also only applicable to white iron, and hence necessitated a preliminary *refining* of the metal when grey iron was employed. This was carried out in the furnace shown in vertical section and plan in Figs. 165 and 166. The metal was charged along with a sufficient quantity of coke on to the hearth A, and there melted and exposed to the blast from six tuyères. When the oxidation had proceeded far enough to reduce the percentage of silicon to the requisite point, the tap-hole was opened, the iron allowed to run into moulds, and the cast-iron cooled by water. The refined iron is highly crystalline, white, and brittle, the carbon being contained in the combined state. The following analyses by Abel of pig-iron, before and after refining, from Königshütte in Silesia, give the different percentages of silicon, phosphorus and sulphur, and show that in this process the silicon is largely eliminated, whilst sulphur and phosphorus are less affected; the total amount of carbon moreover is not much altered.

	Pig-iron.	Refined-iron.
Silicon	4·66	0·62
Phosphorus	0·56	0·52
Sulphur	0·04	0·03

The slag obtained in this process, known as *refinery-slag*, forms, when cold, a dark crystalline mass, with an almost metallic lustre. It consists chiefly of ferrous silicate Fe_2SiO_4, in which, however, a part of the iron may be replaced by manganese, calcium, magnesium, &c. Not infrequently distinct crystals of olivine, $(Mg,Fe)_2SiO_4$, have been found.

The refined iron was then melted on the bed of a reverberatory furnace and stirred by means of iron instruments, so as to expose it thoroughly to the air. As soon as the oxidation had been carried out to a sufficient extent, the metal was removed and treated as already described.

The Modern Puddling Process.—In England and other countries where grey pig is largely made, the preliminary process of refining has been done away with, and the pig-iron is at once submitted to the operation of puddling without previous refining, the process being termed "pig-boiling."

An ordinary puddling furnace is shown in elevation, section,

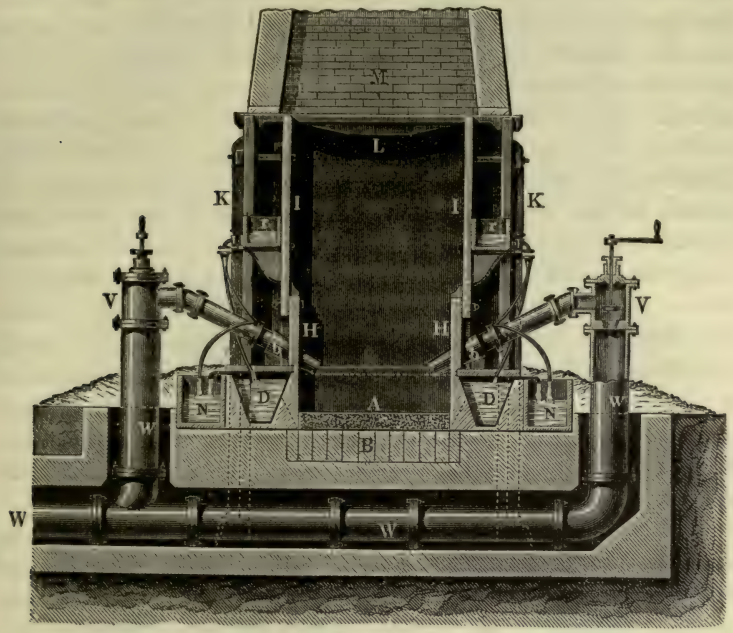


FIG. 165.

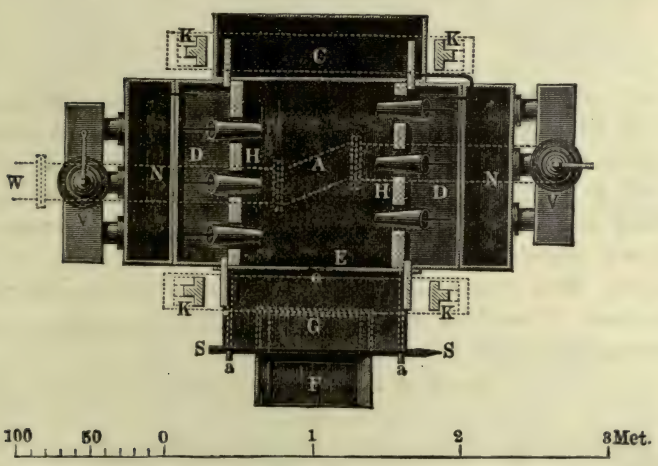


FIG. 166.

and plan in Figs. 167, 168, 169. The bed or hearth of the furnace (*h*) is supported by a cast-iron plate; at each end of

the hearth, which is usually 6 feet long, is a wall built of firebrick, one end being called the fire-bridge (*b*), and the other the flue-bridge (*d*). The bottom and side plates of the hearth are lined with a coating of tap-cinder, which is heated until it becomes soft, and is then spread evenly over the floor of the hearth. Above this is placed a coating or "fettling" of ferric oxide of about $1\frac{1}{2}$ inches in thickness, and this is renewed from time to time as it wears away. Neither of these coatings is shown in the figures. The fire-bars, which are sometimes placed in a slanting position, are seen at (*r*), and the area of the grate should be from one-half to one-third of that of the bed. A powerful draught is obtained by means of a brick chimney, the top of which is furnished with a damper, which can be opened and shut at will by the workman by means of a handle, and thus the passage of air through the furnace regulated. In some furnaces gas is employed with a Siemens' regenerator, and in America, petroleum, or even the gas from the petroleum springs, has been used as a source of heat.

The distinguishing feature of the modern process consists in the fact that the iron is fused in contact with the oxides of iron which are present in the fettling, and with a fusible slag which is added to each charge. In this way the oxidation of the carbon, &c., is mainly carried out at the expense of the oxygen of the fettling, and since an equivalent amount of metallic iron is thus produced the loss is rendered much smaller. In some cases, indeed, the malleable iron produced weighs more than the original pig. The time required for the oxidation is also greatly lessened, the whole operation only lasting two hours. As soon as the charge has been completely melted, it is well stirred, so that it is thoroughly exposed to the action of the fettling and of the air. It is then allowed to cool somewhat and well mixed, whilst in a pasty state, with the oxide of iron present. This brings about the oxidation of the carbon with formation of carbon monoxide, probably according to the equation

$$Fe_2O_3 + 3C = 2Fe + 3CO,$$

and the escape of this gas causes the whole mass to swell up or "boil." The iron then gradually subsides a little into a porous mass, or as it is termed "comes to nature," and is worked into balls which are removed from the furnace and hammered to get rid of the fusible slag and to weld the porous iron into a

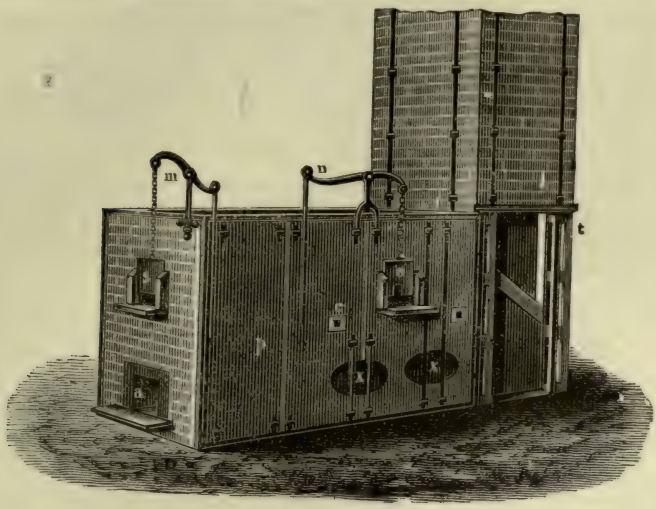


FIG. 167.

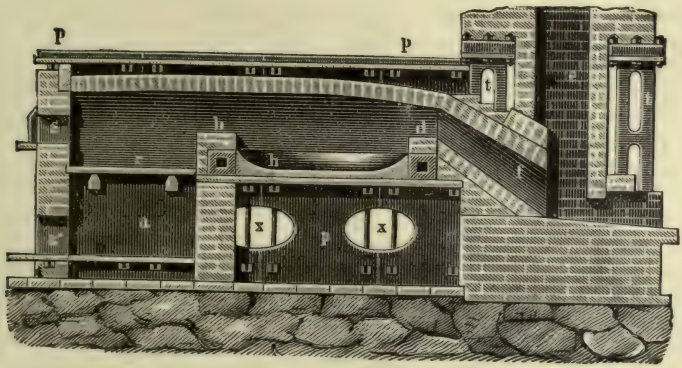


FIG. 168.

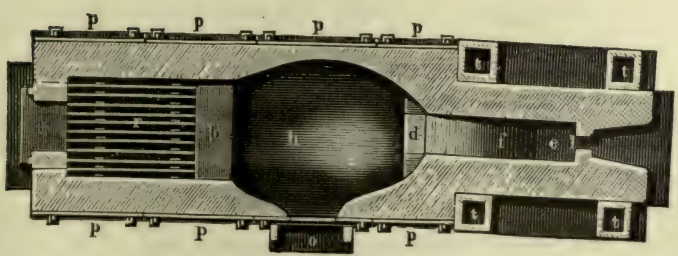


FIG. 169.

homogeneous mass, this process being completed by passing the metal through the rolling mill. It is to this treatment that the characteristic fibrous structure of the wrought iron is due.

Mechanical Puddling Process.—In order to avoid the heavy manual labour necessary in the ordinary puddling processes, revolving puddling furnaces have been invented by Danks, Crampton and others. The construction of these furnaces is somewhat similar to that of the revolving black-ash furnace, but they have not been generally adopted.

541 The following analyses made by J. G. Snelus give an idea of the consecutive chemical changes which take place in the passage from cast- to wrought-iron: (*a*) is the mottled Cleveland iron which was puddled in the Danks revolving furnace; (*b*) a portion taken out when melted; the composition ten minutes later is shown by (*c*); after a lapse of twenty minutes by analysis (*d*); the composition of the bloom is shown in (*e*); and the puddled bar in (*f*): α C stands for combined carbon, and β C for graphite:

	Fe.	αC.	βC.	Si.	P.	S.	Mn.
a . .	93·19	1·45	1·38	1·24	1·49	0·11	0·63
b . .	95·03	2·83	—	0·82	0·91	0·09	—
c . .	96·46	2·80	—	0·20	0·58	—	—
d . .	98·09	1·17	—	0·05	0·52	—	—
e . .	98·40	0·15	—	0·09	0·45	—	—
f . .	97·13	0·15	—	0·14	0·47	0·04	0·14

It will thus be seen that the silicon is first burned out along with most of the manganese and phosphorus, whilst the carbon afterwards disappears.

Almost the whole of the phosphorus contained in the pig is found in the slag or *tap-cinder* as phosphide and phosphate; the sulphur is left in the cinder as iron sulphide. The tap-cinder is rich in iron, and is difficultly reducible; but it is nevertheless employed for the manufacture of a common kind of iron. The following analyses of tap-cinder give an idea of the composition of this material:

Analyses of Tap-Cinder.

SiO_2.	FeO.	MnO.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	P_2O_5.	S.	Analyst.
7·71	66·32	1·29	8·27	1·63	3·91	0·34	8·07	1·78	Riley.
11·76	58·67	0·57	17·00	2·84	2·88	0·29	4·27	3·11	,,
29·60	48·43	1·13	17·11	1·28	0·47	0·35	1·34	1·61	Percy.

542 *Properties of Malleable Iron.*—Good hammered and rolled bar-iron, when it contains from 0·15 to 0·3 per cent. of carbon possesses a fibrous texture, but when the amount rises to 0·5 or above it possesses a granular or crystalline structure. Fibrous iron is soft and possesses a grey colour; granular iron is harder and has a dead silvery lustre. The hardness of iron increases with the amount of carbon. Malleable iron melts at from 2,100° to 1,900°, according to the amount of carbon which it contains. The physical properties of commercial malleable iron vary widely, being largely influenced by the nature and amount of the impurities which the iron contains; thus, for instance, sulphur imparts to iron the property of becoming brittle whilst hot, or, as it is technically termed "red-short," whilst phosphorus renders iron weak at the ordinary temperature, when the iron is said to be "cold-short." Cold-short iron exhibits a peculiar fracture, and the property of cold-shortness apparently depends upon a peculiar crystalline condition of the iron, so that it appears probable that the method of manufacture as well as the percentage of phosphorus has an influence in producing this defect. The lower the temperature at which the puddling takes place the more easily is the phosphorus got rid of, since at a high temperature the iron takes up phosphorus from the phosphates contained in the siliceous slags.

Silicon exerts an influence similar to that of carbon, making the iron harder and more easily fusible and diminishing its tenacity. Manganese prevents this action, and, in the puddling process, assists the removal of sulphur and silicon. Copper in a larger proportion than 0·5 per cent. produces red-shortness, and arsenic increases the brittleness and reduces the welding power, as well as the tenacity of the iron.

(III.) The Manufacture of Steel.

543 Steel was obtained in early times directly from the ore in a similar manner to malleable iron.

Homer sings—

> And as when armourers temper in the ford,
> The keen-edged pole-axe, or the shining sword,
> The red-hot metal hisses in the lake;
> Thus in his eyeballs hissed the plunging stake.
>
> Pope's *Odyssey*, book ix.

These remarks evidently apply to steel, as wrought-iron cannot be thus tempered. The Chalybes on the coast of the Black Sea were renowned for their ability in working the iron ores into steel, and the Greek name for steel, χάλυψ, appears to have been derived from the name of this tribe.

The older chemists looked upon steel as a peculiarly pure form of iron, and "Basil Valentine," in his *Last Testament*, terms it the "hardest, purest, most malleable iron." Lemery held peculiar views respecting steel. In his *Cours de Chymie*, published in 1675, he says: "Le fer est un métal fort poreux, composé de sel vitriolique, de soulfre et de terre mal lié et digéré ensemble. On le réduit en acier par le moyen des cornes ou des ongles d'animaux, avec lesquelles on le stratifie et ensuite on le calcine; ces matières contenant beaucoup de sel volatile qui est alcali, tuent les acides de fer qui tenoient ses pores ouverts, et les rendent plus compacte."

Stahl considered iron to be an impure metal containing earthy materials, whilst steel was the pure metal saturated with phlogiston. Similar views were held by the later chemists. Bergman was the first to distinguish chemically between wrought-iron, steel, and cast-iron. He found that the first when dissolved in acids yielded the largest quantity of inflammable air, steel somewhat less, whilst cast-iron gave the smallest quantity; hence he concluded that steel contained less phlogiston than wrought-iron. He also showed that cast-iron contained more graphite than steel, and this more than wrought-iron, and hence he concluded that cast-iron was converted into steel by loss of graphite and by absorption of phlogiston, whilst he supposed that when steel was produced from wrought-iron the opposite reactions occurred. Rinnman in 1782 developed similar views, and he especially insisted that malleable iron was a perfect metal, and was converted into steel by absorption of phlogiston, but that this phlogiston was not the substance usually thus designated, but plumbago. In 1786 Monge, Vandermonde and Berthollet published a research proving that the difference between the various kinds of iron is mainly determined by the variation in the amount of carbon which they contain, but the many doubtful points which remained were only cleared up by the comprehensive researches of Karsten and Sefström.[1]

As already explained (p. 944), the amount of carbon present has now been found not to provide a convenient distinction

[1] Percy, *Iron and Steel*, p. 116.

between malleable iron and steel, since specimens of these may contain the same amount of carbon and yet possess very different properties, owing to the difference in their internal structure.

Steel can be made in a very large number of different ways, the principles of which may be roughly summarised under the following heads:—

A. Directly from the ore.
B. From malleable iron.
   1. By simple fusion.
   2. By the direct addition of carbon, accompanied or followed by fusion.
   3. By fusion accompanied by the addition of more highly carburetted metal.
C. From cast-iron.
   1. By the removal of carbon.
   2. By the addition of a less highly carburetted metal, such as malleable iron.

Many of the processes actually adopted involve two or more of these methods, and the number of different processes now employed is very large, but only two or three of the most important and typical methods are here described.

544 *The Cementation Process.*—Forty-five years ago the only method by which steel could be made was the decarburisation of the cast-iron in the puddling furnace, and the subsequent re-carburisation of the puddled bar by the cementation process. The product was then either fused in a crucible, yielding cast-steel, or drawn out under the hammer, whereby tilt-steel or shear-steel was obtained.

The cementation method of preparing cast-steel is mentioned by Agricola in his *de re Metallica*, whilst that of hammered or tilt-steel was first described by Réaumur in 1722.

In the manufacture of steel by the cementation process carbon is added to the otherwise pure wrought-iron. This is carried on in the furnace shown in Figs. 170 and 171. Into the furnace are built two square boxes, or "converting pots," c c, Fig. 171, of infusible fire-brick; and into these are placed the bars of iron which are to be converted into steel. The flames from a fire placed in the hearth (*g*) play round these boxes. The iron which has to be converted into steel is usually in the form of straight bars about 3 inches (75 mm.) broad,

and 0·75 inch (18 mm.) thick, which are somewhat shorter than the converting pot into which they are placed. The interstices between the bars when piled in the pot are filled up with powdered charcoal or soot, technically termed "cementing powder," a thick layer of the charcoal being placed on the top of the bars, and the whole mass plastered over with grinders waste. The total weight of iron contained in each box is from five to six tons. The fire is gradually raised to a full red-heat, or to about the melting point of copper, and is maintained at this point for about from seven to ten days, according to the quality of steel which is needed. Spring-steel requires seven days, shear-steel eight days, and steel for welding from nine to

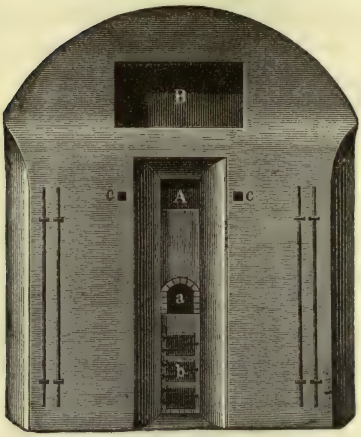


Fig. 170.

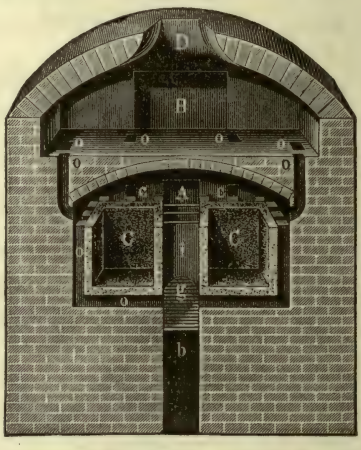


Fig. 171.

ten days. During the operation trial bars are removed by the openings (c) from the ends of the chests, and when it is found that the bar-iron has been completely converted into steel the furnace is allowed to cool, and after several days the charge is removed. The steel bars thus obtained retain the form of the original iron, but in physical properties they differ considerably from the original. Thus the coloured surface of the fractured bar of steel has no longer the bluish tint of malleable iron, but has acquired a reddish tint, not very different from that of bismuth, and the texture has become distinctly crystalline. The steel is also much more fusible than malleable iron, and a varying amount of carbon has been taken up.

The following is an analysis by David Forbes of cementation-steel made at Sheffield from Swedish iron:

Combined Carbon.	Graphitic Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
0·627	0·102	0·030	0·005	0·000	0·120

An English cement-steel was found by Berthier to contain 1·87 per cent. of total carbon, and 0·10 per cent. of silicon, the remainder being iron.

A remarkable alteration of the surface is likewise noticed in the passage of wrought-iron into steel, it being covered with blisters or blebs, and hence it is termed *blister-steel.* The formation of these blisters is undoubtedly due to the production of gas within the bar, but the exact nature of this gas is somewhat doubtful. Probably it arises from the combination of a part of the carbon with oxygen derived from particles of oxide of iron contained in the interior of the bar. The bars are finally cut up, sorted according to their quality as indicated by the fracture, melted in plumbago crucibles, and finally cast in ingots.

Various hypotheses have been proposed to account for the phenomena observed in the cementation process. According to one view, the carbon is absorbed from the exterior and passes to the interior of the bar partly from the solid fuel, partly from the carbon monoxide formed by its partial combustion, and partly from the hydrocarbons derived from the hydrogen contained in the charcoal. The probability of the view that the carbon monoxide is the active agent is strengthened by the fact observed by Graham, that red-hot iron has the power of absorbing from eight to ten times its volume of this gas. Others have assumed that the carburisation is brought about rather by the hydrocarbons than carbon monoxide, and that it is especially effected by the vapours of the potassium cyanide, formed by the action of potassium carbonate and carbon, upon the nitrogen contained in the air still left in the boxes, and in support of this hypothesis it is stated that the cement powder loses its power after it has been used for some time and has lost its alkalis. It is also a well-known fact that the cyanides of the alkali metals have the power of giving up carbon to cast-iron.

It also appears probable that the carburisation of the iron may be due in part, if not altogether, to an actual diffusion of

the solid carbon into the bars, the blister-steel being therefore a "solid solution" of carbon in iron. This phenomenon would then be analogous to the inter-diffusion of metals in the solid state which has been described by Roberts-Austen (p. 68).

545 *Crucible Steel.*—The cast-steel made by melting cemented bars in a graphite crucible is of excellent quality, and is employed for the best classes of cutlery. Many other qualities of steel may also be obtained by the use of crucibles as already indicated; iron of various qualities being melted with carburising or decarburising materials, or with iron of a different carbon content.

One of these processes, suggested by Karsten, but first carried out on the large scale by Krupp of Essen, consists in fusing pure wrought-iron with the requisite quantity of spiegel. The progress which was made in the manufacture of cast-steel by this process is illustrated by the fact that one of Krupp's cast-steel six-pounder guns, exhibited in 1851, was considered a marvel, whilst in 1873 the same firm exhibited, in Vienna, a cast-steel block weighing 52,500 kilograms, for the purpose of casting which 1,800 melting-pots, each holding thirty kilos. of steel, were employed.

In other cases malleable iron is melted with charcoal, or with cast-iron; or again, cast-iron is melted with iron ore. In all cases the molten metal cannot be immediately poured into the ingot mould, as the castings produced would then be full of vesicles. It is therefore allowed to remain in tranquil fusion for some time before pouring, or ferro-aluminium is added, and the metal at once poured. The castings are then found to be sound and free from vesicles.

546 *Bessemer Steel Process.*—Since the year 1856 a complete revolution has taken place in the iron industry, and this has mainly been caused by the discovery of a method for manufacturing cast-steel, on the large scale, from cast-iron. This discovery was made by Bessemer,[1] and first communicated in a paper read before the Mechanical Section of the British Association, at its Cheltenham meeting, in 1856, and entitled "The manufacture of malleable iron and steel without fuel." The process consists in removing the carbon, silicon, and manganese contained in cast-iron by oxidising them by means of a blast of air blown through the molten metal, the heat evolved by the oxidation being sufficient to keep the whole in a liquid

[1] Patent, Dec. 7, 1855. No. 2768.

state until the cast-iron is converted into steel, which is thus effected without the intermediate laborious and costly processes of puddling and cementation. The first experiments which were made were unsuccessful, for although by this process the carbon and silicon can be removed, the phosphorus and sulphur which are contained in the pig remain in the finished steel, and for this reason the ordinary impure English cast-iron yielded unsatisfactory results. The case, however, was otherwise when the pure Swedish charcoal-pig was used; indeed the first real success in working the process was achieved with this iron at the Högbo Ironworks, at Sanviken, and this was followed by the successful use of grey-iron made from the Ulverston hæmatite, and now technically known as *Bessemer-pig*. Other difficulties then arose such as the too complete oxidation, when the whole of the carbon is burnt out, a mass of pasty wrought-iron being produced instead of liquid steel. This was overcome by the important suggestion made by Mushet,[1] of the addition of spiegel at the end of the operation in such quantity as is necessary for the conversion of the whole of the wrought-iron into steel.

The oxidation is carried on in an egg-shaped vessel, termed the converter (Figs. 172, 173), made of wrought-iron plates bolted firmly together and lined with an infusible siliceous rock termed gannister which is ground, moistened with water and applied in the form of a paste to the interior. The lower portion is an interchangeable bottom, consisting of a shallow lower section of the vessel with tuyère-box or wind-box and tuyères, together with the necessary arrangements for fixing these in their places. This bottom is attached to the vessel in such a manner that the narrow space between it and the vessel lining may be rammed with plastic gannister by men working outside of the vessel, and this joint can be easily made at once upon pulling away the old bottom. This arrangement is of great advantage, inasmuch as by its use the number of blows per diem can be considerably increased. The pig-iron, which must be free from phosphorus and sulphur, is first melted in a cupola, and from five to twelve tons of this run into the converter, either directly from the cupola or from an intermediate ladle, the mouth of the converter being lowered to the proper angle to receive the molten metal. The converter is then gradually raised to the vertical position; at the same time a moderate blast of air is forced through the

[1] Patent, Sept. 22, 1856.

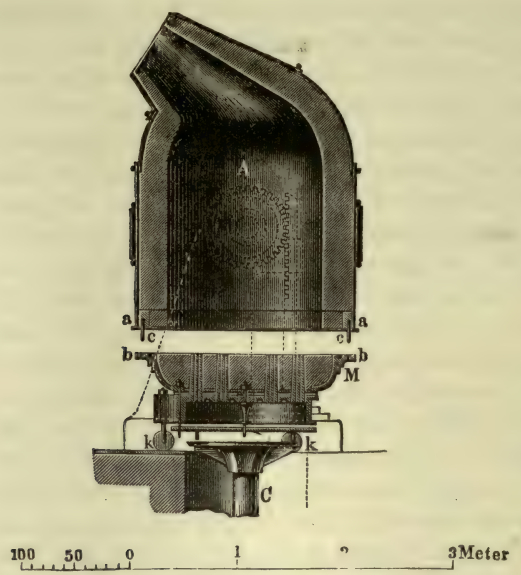


FIG. 172.

tuyères by means of the pipes L N and D, the pressure of the blast being afterwards raised to from eighteen to twenty pounds per square inch.

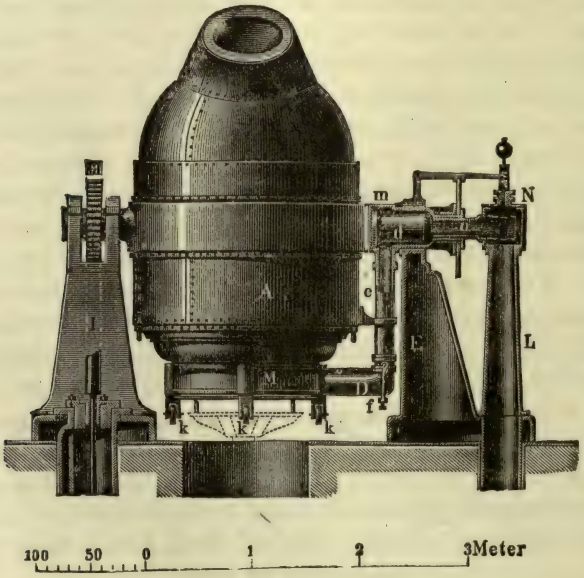


FIG. 173.

The combustion of the silicon, manganese, and carbon, as also of a portion of the iron, then begins, and the temperature rises to a point sufficiently high to keep the metal liquid. In the first part of the blow the graphite is converted into combined carbon, and a highly siliceous slag is formed, a portion of the silica being derived from the lining. When the first period is complete, an orange-yellow flame edged with blue appears at the mouth of the converter, and the second period termed the "boil" then begins. In this, the slag containing oxide of iron oxidises the carbon, with formation of carbon monoxide which escapes throughout the mass giving to it the appearance of a boiling liquid. During this period particles of the slag and molten iron are thrown out from the mouth of the converter, and a very brightly luminous flickering flame makes its appearance, accompanied by a rapid stream of sparks due to the combustion of the particles of iron. After the lapse of from six to eight minutes the intensity of the action diminishes, the shower of sparks ceases, and suddenly the flame disappears or is said to drop. The whole of the carbon has now been oxidised, and if the blast be left on the combustion is continued at the expense of a portion of the iron. Hence, the force of the blast is now lessened, the converter inclined, then the blast stopped, and the requisite amount of fluid spiegel or ferromanganese introduced to bring the steel to the requisite degree of carburisation. The blast is then turned on again for a few seconds, or the mixture is simply allowed to stand for a short time, and the whole mass poured out into the ladle. After standing for a few minutes in the ladle the fluid steel is cast into ingot moulds, and the cast-steel worked up under the hammer and in the rolling mill. The whole process lasts from twenty to thirty minutes, and in this time from five to twelve tons of cast-iron are converted into nearly the same weight of cast-steel.

Figs. 174 and 174A show one form of arrangement for carrying on the Bessemer process. The two converters (AA) are charged with molten pig from the cupola furnaces (BBB), the molten spiegel needed at the end of the operation being obtained from the smaller furnaces (CC). The fluid steel is poured from the converter into the ladle (G) which can be elevated and carried round the semicircular pit by mean of the hydraulic crane (D). The steel flows from an opening in the bottom of the ladle into the ingot moulds (LL). In order to prevent the formation of bubbles which occur when the steel is run directly into these

moulds, an arrangement (shown at M) is employed by which the liquid metal is allowed to run in at the bottom of the mould.

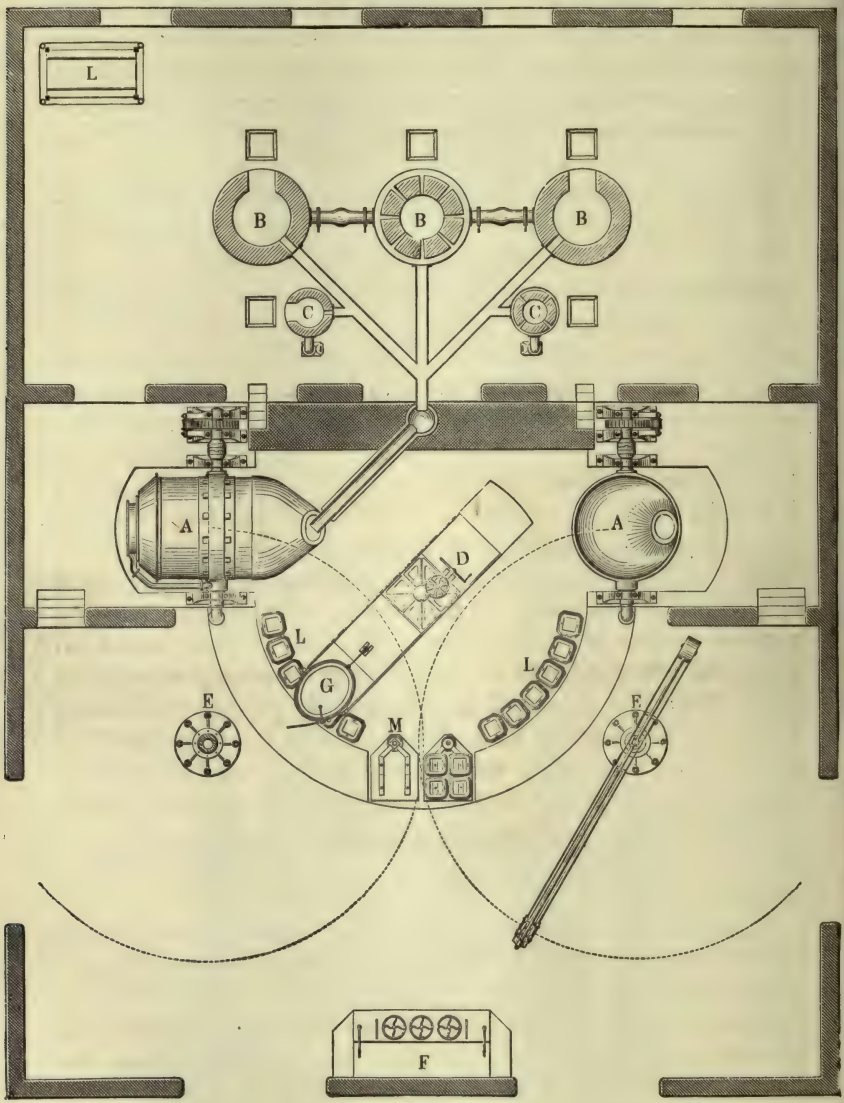


FIG. 174.

The steel-ingots after cooling are removed by means of the long-armed hydraulic cranes (EE), and the whole of the movements of

the converter, ladle and cranes are controlled by the foreman by working the wheels (F).

The arrangement of Bessemer plant, especially that designed by Holley, has reached its perfection in the United States, where the output from one converter greatly exceeds that found practicable elsewhere,[1] the molten iron being run directly from the blast furnace into the converter. In Sweden, fixed converters with tuyères at the side are employed; the iron which

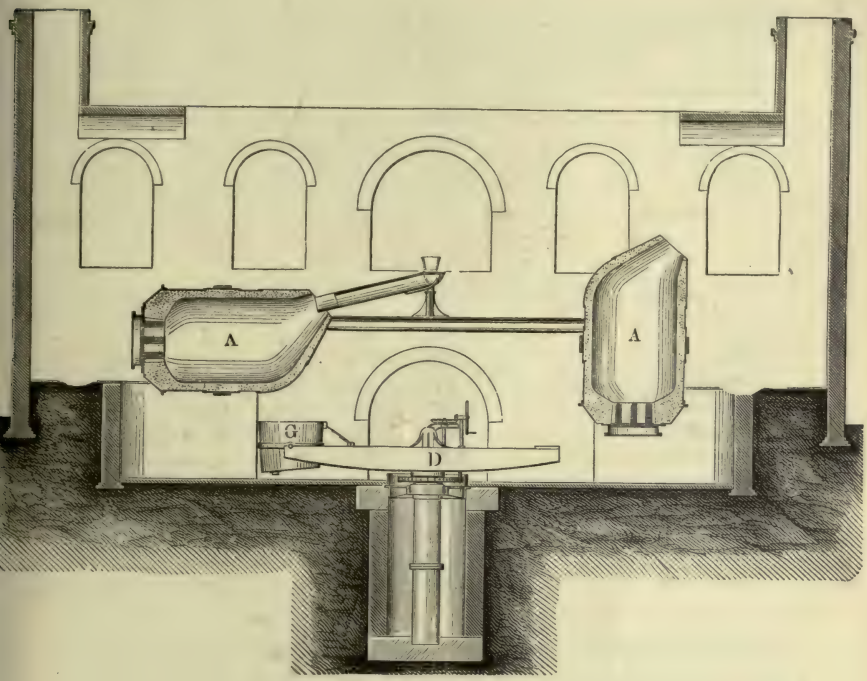


FIG. 174A.

is used is a pure magnetic charcoal iron, and the decarburisation is carried on in the converter to the exact point needed to produce steel, this point being determined by an examination of the flame.

547 The chemical changes which the cast-iron undergoes in the various stages of the Bessemer-process, as well as the composition of the slags obtained, are exhibited in the following table:

[1] For complete description, see *Engineering*, March 9 and 16, 1867.

(*a*) Composition of the pig-iron used (3,517 kilos.). (*b*) After the first period of twenty-eight minutes blow. (*c*) After the second period of seven minutes blow. (*d*) After the third period of three minutes blow. (*e*) Finished steel (3,058 kilos.) after the addition of 168 kilos. of spiegel.

Composition of Bessemer-metal. No. 1.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	3·180	—	—	—	—
Chem. comb. carbon	0·750	2·465	0·909	0·087	0·234
Silicon	1·960	0·443	0·112	0·028	0·033
Phosphorus	0·040	0·040	0·045	0·045	0·044
Sulphur	0·018	trace	trace	trace	trace
Manganese	3·460	1·645	0·429	0·113	0·139
Copper	0·085	0·091	0·095	0·120	0·105
Iron	90·507	95·316	98·370	99·607	99·445

Composition of Bessemer-slag.

	a.	*b.*	*c.*	*d.*	*e.*
Silica	40·95	46·78	51·75	46·75	47·25
Aluminia	8·70	4·65	2·98	2·80	3·45
Ferrous oxide	0·60	6·78	5·50	16·86	15·43
Manganous oxide	2·18	37·00	37·90	32·23	31·89
Lime	30·36	2·98	1·76	1·19	1·23
Magnesia	16·32	1·53	0·45	0·52	0·61
Potash	0·18	trace	trace	trace	trace
Soda	0·14	trace	trace	trace	trace
Sulphur	0·34	0·04	trace	trace	trace
Phosphorus	0·01	0·03	0·02	0·01	0·01

The following tables contain analyses of two other series of samples of Bessemer-metal, taken at the end of each period of the process. As in the first Table, (*a*) represents the pig, and (*e*) the finished steel.

Composition of Bessemer-metal. No. 2.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	2·519	—	—	—	—
Chem. comb. carbon	1·000	3·040	1·640	0·190	0·370
Silicon	2·260	0·955	0·470	trace	trace
Phosphorus	0·073	0·070	0·070	0·070	0·059
Sulphur	0·107	0·091	0·098	0·093	0·090
Manganese	0·410	—	—	—	0·649

Composition of Bessemer-metal. No. 3.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	2·070	—	—	—	—
Chem. comb. carbon	1·200	2·170	1·550	0·097	0·566
Silicon	1·952	0·759	0·635	0·020	0·030
Phosphorus	0·048	0·051	0·064	0·067	0·055
Sulphur	0·014	trace	—	—	—
Manganese	0·086	—	—	—	—
Copper	—	—	—	—	0·039

Analyses No. 2 were made by Baker, at the Atlas Works, Sheffield. Analyses No. 3, by Snelus, at Dowlais.

Converter Gases.—Snelus has investigated the composition of the gases issuing from the converter. When the charge lasted eighteen minutes he found the following results on analysis of the gases drawn out at the times after the commencement of the blow given in minutes in the first horizontal column:

	2.	4.	6.	10.	12.	14.
CO_2	10·71	8·59	8·20	3·58	2·30	1·3
O	0·92	—	—	—	—	—
CO	—	3·95	4·52	19·59	29·30	31·11
H	88·37	0·88	2·00	2·00	2·16	2·00
N		86·58	85·28	74·83	66·24	65·55

Elimination of Phosphorus.—It was at first supposed that the non-elimination of phosphorus in the Bessemer-process was due to the high temperature and that if the process could be conducted at a lower temperature, as in puddling, all the phosphorus would be found in the slag. Messrs. Thomas and Gilchrist[1] and Snelus have, however, proved that it is possible completely to eliminate phosphorus in the Bessemer-process by using a basic lining of calcined dolomite for the converter instead of the usual siliceous one, phosphate of lime and magnesia being produced. This is known as the "basic" process, and is now largely in use in the case of phosphorus-pig; it constitutes one of the most important advances in metallurgy, since it renders possible the direct production of steel from ordinary pig-iron, such as Cleveland pig, which contains comparatively large quantities of phosphorus.

The process is carried out in the main like the ordinary Bessemer-process, but differs from it in one or two points. A certain amount of lime is placed in the converter and heated by

[1] *Proc. Iron and Steel Institute*, 1878.

the combustion of a small quantity of coke before the molten pig is run in. The blow is then conducted in the ordinary way, but when the flame has dropped the blow is continued, and it is in this "after blow" that the phosphorus is chiefly removed. This is well shown in the following table, which gives the results of a "blow" by the basic process: (*a*) gives the composition of the Cleveland pig, (*b*) after five minutes blow, (*c*) after ten minutes, (*d*) after fifteen minutes, (*e*) after eighteen minutes. As soon as the phosphorus has been removed, a point which is indicated by the appearance of the fracture of a small sample of the metal, the process is concluded in the usual way by the addition of spiegel or ferromanganese. The slag, which contains the whole of the phosphorus in the form of phosphate, is now ground and sold as a valuable manure.

	a.	*b.*	*c.*	*d.*	*e.*
Carbon	3·50	3·55	2·35	0·07	trace
Silicon	1·15	0·50	0·09	trace	0·00
Manganese	0·71	0·56	0·27	0·12	trace
Phosphorus	1·57	1·60	1·43	1·22	0·08
Sulphur	0·16	0·14	0·13	0·12	0·10

Application of the Spectroscope to the Examination of the Bessemer Flame.—It has already been stated that the point at which the flame drops is that at which it is found by practice to be necessary to stop the blast, but it is not always easy to hit this point with accuracy; and if the blow be stopped a few seconds too soon, or carried on for a few seconds too long a time, the quality of the resulting steel suffers. The application of the spectroscope to the determination of this point was made by Roscoe in 1863,[1] and has since been investigated by Watts, Lielegg, Snelus, Hartley, and others. It appears from these experiments that the point of complete decarburisation can be most exactly and easily determined by the sudden disappearance of certain absorption-bands observed in the spectrum of the flame. These bands, however, are not due in themselves to carbon, but to the presence of the oxides of manganese (Watts), the disappearance of this metal from the molten steel being simultaneous with that of the carbon.

548 *Other Methods of Steel-Making.*—Of these, that known as the Siemens-Martin process is one of the most important. The steel is produced in a reverberatory furnace by melting cast-iron and then adding to it malleable iron in the form of scrap

[1] *Phil. Mag.* 1863, 5318.

or iron ore, or, more usually, both of these. The process is usually carried out with an acid (siliceous) lining to the hearth, but if pig-iron containing phosphorus be used, a basic lining of dolomite must be employed.

Figs. 175, 176, and 177 represent a Siemens' 12-ton regenerative steel-melting furnace for producing cast-steel according to the Siemens-Martin process. Fig. 175 gives the vertical section, Fig. 176 the side elevation, and Fig. 177 a transverse section through the line AB Fig. 175. The gases from the producer (see Fig. 176) pass along the iron downcast wrought-iron tube, G and G′, Fig. 176, to the valve V, which can be directed by means of the handles A, so as to pass either into the chamber C or the chamber C′, Fig. 175, where it takes up the heat previously imparted to the bricks by the waste gases. Having thus been heated it passes into the furnace by the flues, meeting with the requisite quantity of air, which has previously been similarly heated by passing through similar chambers, D or D′, and which enters by the upright flues F. The gas and air thus leaving the flues mingle and burn, and the flame passes over the hearth of the furnace (*k*), made of infusible sand contained in an iron casing. Supposing that the gas and air are passing through the chambers C and D, the flame passes over the hearth, and the heated waste gases find their way through the flues F′ into the chambers C′ and D′, where they heat up the bricks to full whiteness. As soon as this is accomplished, the temperature of C and D being proportionately lowered, the gas valve V, Fig. 176, and the air valve V′, Fig. 177, are reversed, and the currents of gas and air are thus turned into the freshly heated chambers C′ and D′, whilst the cooled chambers C and D are in their turn heated by the waste gases from the furnace. As the temperature of this furnace is extremely high the sides and top of the furnace and the flues exposed to the action of the strongly-heated gases require to be made of the most infusible materials; for this purpose silica bricks are used.

The proportion of cast-iron and wrought-iron scrap employed for the furnace-charge varies according to the kind of steel required. This, after being well melted, is run out by means of the spout into the ladle into which the necessary quantity of ferromanganese or spiegel has been placed. The steel is then ready for casting.

The ordinary Bessemer ingots are frequently found to be honeycombed and unsound from the presence of air bubbles, and

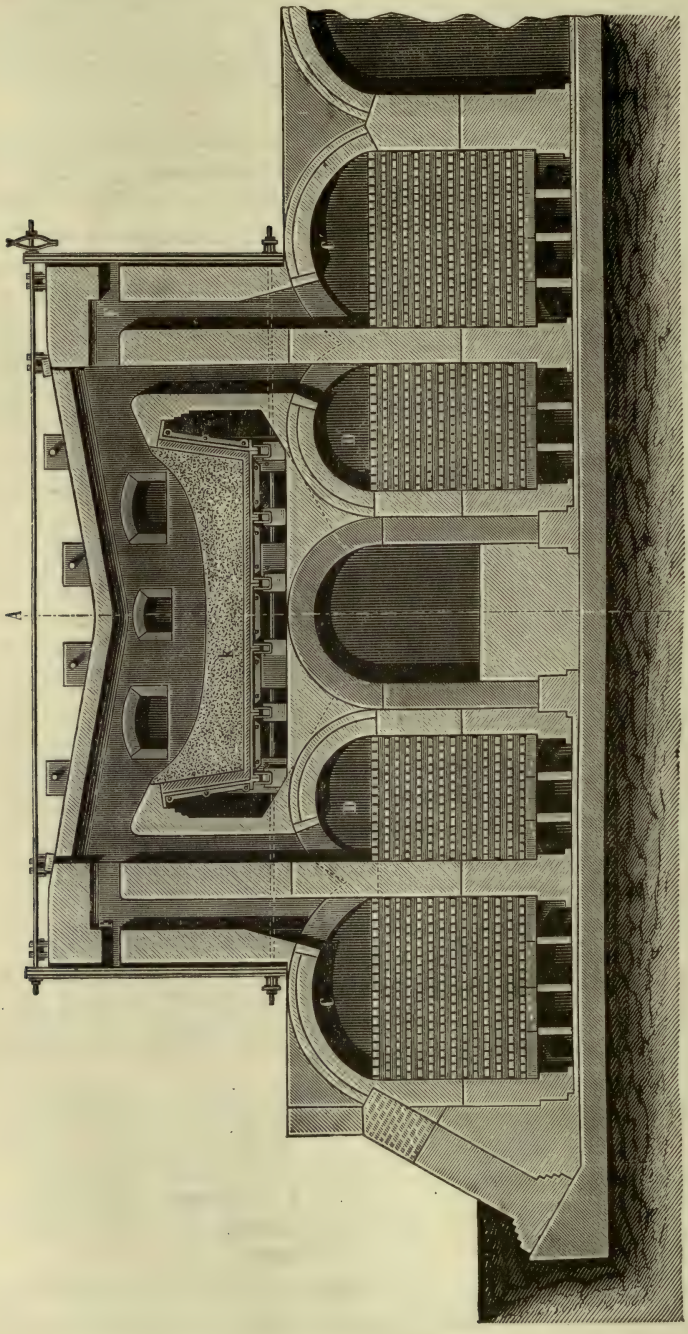


FIG. 175.

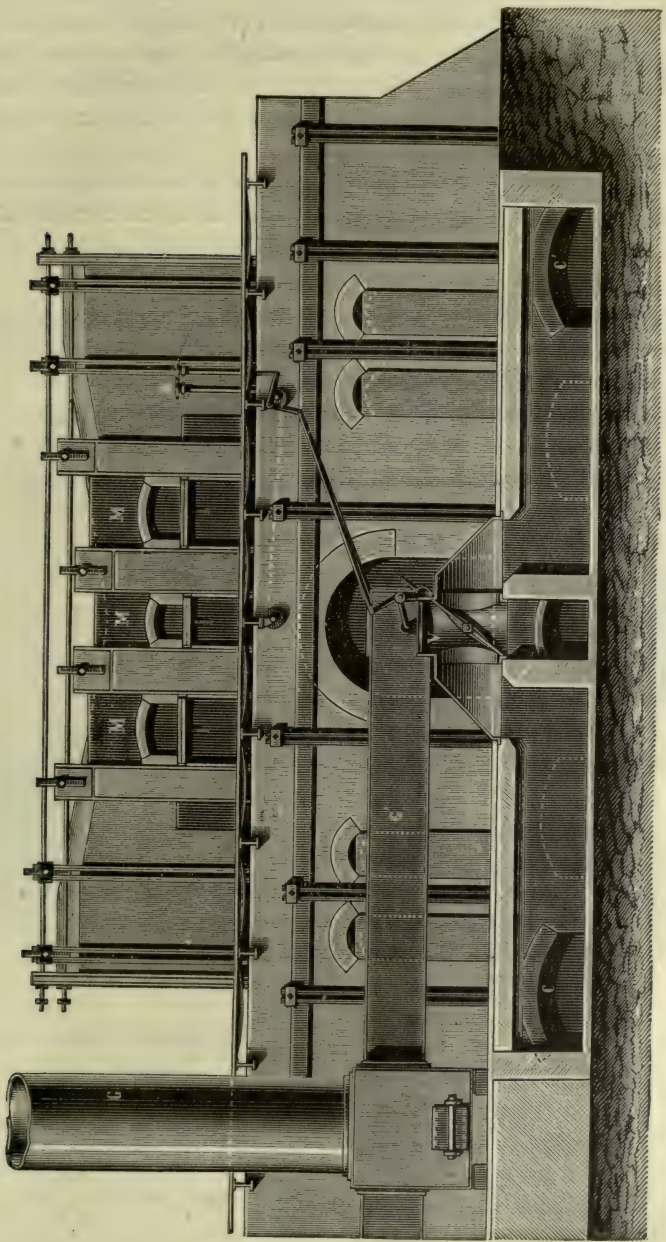


Fig. 176.

the same thing is noticed in all large steel castings. In order to obtain perfectly homogeneous steel Sir Joseph Whitworth exposes the molten steel during its solidification to enormous pressure by means of hydraulic machinery. By this means the metal gains in tensile strength and elasticity as well as in homogeneity.

Many modifications and adaptations of the open hearth process are now in use. Among these may be mentioned that carried out

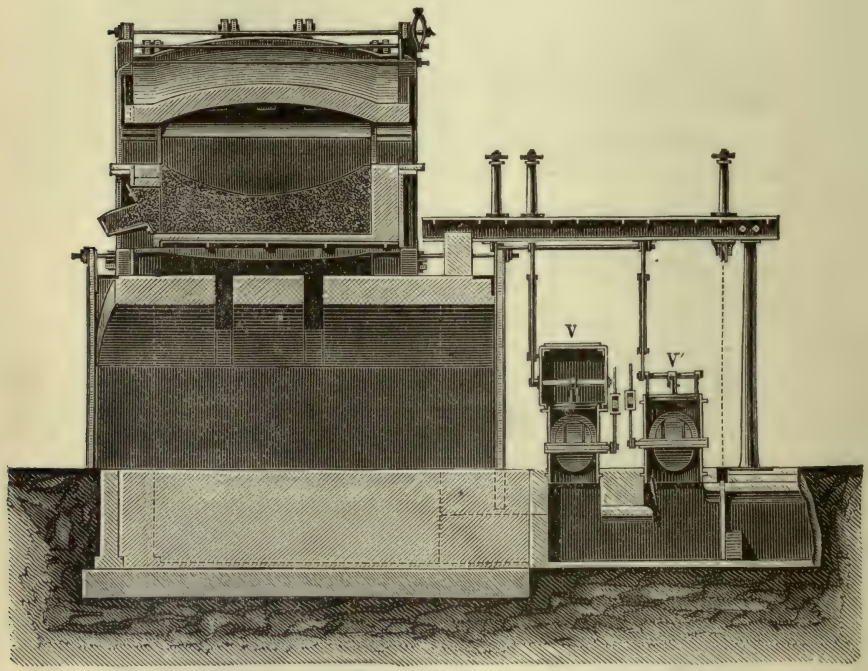


Fig. 177.

by Kupelweiser at Witkowitz. In this process the molten phosphoric pig is run straight from the blast furnace into an ordinary acid-lined Bessemer converter, and there half blown, the silicon being thus removed. It is then run on to a basic hearth, lined with a special variety of dolomite, and there treated in the usual way, the result being that much more equable working is obtained.

Pernot's Revolving Hearth.—As the puddling of iron is greatly facilitated by mechanical agitation, an arrangement for effecting

a similar agitation in the bath of an open-hearth steel-furnace has been suggested and carried out by Pernot. The general arrangement of the furnace is shown in Fig. 178. It differs from the Siemens-Martin in having a circular hearth supported on a trolley, by means of which the bottom may be drawn out for re-lining or for other purposes. The hearth revolves on an axis, inclined about 6° to the vertical, thus effecting an intimate mixture of the molten metal, and thoroughly exposing it to the action of the flame. The speed of rotation is three revolutions

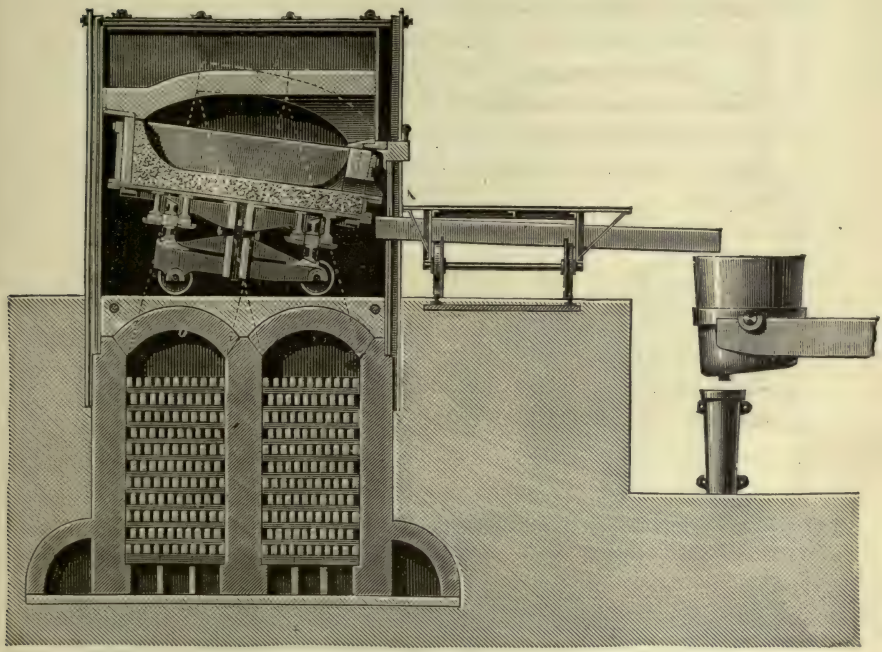


Fig. 178.

per minute. A hearth for a 10-ton charge is lined up to $8\frac{3}{4}$ feet in diameter, and is 21 inches deep, the arrangement of the regenerators being the same as in the ordinary Siemens. This furnace is used in France, and it is claimed that time is saved and that the steel is more uniform than that made by the ordinary plan. When the process is complete the molten metal is allowed to run into the ladle from which it is passed into the ingot moulds.

Lastly *wootz* or Indian steel must be mentioned. This is

a product prepared by heating malleable iron in small clay crucibles, in which small pieces of the wood of *cassia auriculata* are also placed, until the external portions begin to fuse. The product is then hammered frequently and the steel thus consists of a mixture of two irons, one being rich and the other poor in carbon.

Indian wootz is extremely hard and elastic, and was highly prized by the ancients. A specimen of wootz was sent from Bombay to the President of the Royal Society, and the first description of the substance was given by Dr. Pearson in 1795,[1] and the steel was afterwards analysed by Faraday and Henry. It was at one time believed that wootz owed its special valuable properties to the presence of a small quantity of aluminium, but this has not been confirmed by subsequent analysis.

The following analyses serve to show the composition of steel of various kinds. Analyses of Bessemer steel have already been given.

Analyses of Steel.

	αC.	βC.	Si.	P.	S.	Mn.	Cu.	Co & Ni.
No. 1.	1·129		trace	—	trace	—	trace	—
„ 2.	0·627	0·105	0·030	—	0·003	0·120	—	—
„ 3.	1·180		0·330	0·020	—	trace	0·300	0·120
„ 4.	0·501		0·106	0·096	0·002	0·144	—	—
„ 5.	1·336	0·312	0·043	—	—	—	—	—

No. 1. Styrian refinery steel.
No. 2. English cast-steel, from blister-steel.
No. 3. Krupp's cannon steel.
No. 4. English puddled steel.
No. 5. Indian wootz.

549 *Properties of Steel.*—The most characteristic property of steel is its power of assuming an almost adamantine hardness when quickly cooled, as when plunged into water. After this treatment it is extremely brittle, almost perfectly elastic, and so hard that it cannot be attacked by a file. This hardness and brittleness may be completely removed by annealing, that is to say, heating the steel to a high temperature and then allowing it to cool slowly. It may also be partially removed by a process of tempering which consists in heating the steel moderately and then allowing it to cool. The temper of steel depends upon the heat to which the steel is raised, and the workman judges as to the temperature by observing the various colours which the

[1] *Phil. Trans.* 1795, part ii. 322.

surface of the metal assumes during the progress of the operation. The tints thus observed are the colours of thin plates caused by the different thicknesses of the oxide formed on the surface. When the requisite tint is reached the object is quickly cooled by being plunged into water, brine, oil, &c. The hardest temper, such as is required for steel for surgical instruments, lancets, and razors, is that obtained at the lowest temperature; the tint employed for this purpose is that first reached, and is of a light straw colour, the temperature being about 230°. Steel tempered at 243° possesses a full yellow colour, is tougher than the former, and is the tint to which penknives are usually tempered. At 255° a brownish-yellow tint is attained, and steel thus tempered is best fitted for cold chisels and shears for cutting metals. At 265° the first shade of purple shows itself, and this is the temper employed for pocket-knives, axes, and plane-irons. A temperature of 277° gives a purple which is the tint for table-knives and cloth-shears, and for swords and watch-springs the metal is cooled when it has a bright blue colour, corresponding to a temperature of 288°. At higher temperatures, from 290° to 316°, steel assumes a dark blue colour, and is used for shears, chisels, and especially for large saws.

The different degrees of heat may be obtained by dipping the several articles into a bath of fusible metal or oil provided with a thermometer and heated up to the requisite temperature, although in ordinary cases this method is not carried out.

Damascening is produced by repeatedly welding, drawing out, and doubling up a bar composed of a mixture of steel and iron, the surface of which is afterwards treated with an acid. The surface of the iron retains its metallic lustre under the action of the acid, whilst that of the steel is left with a black firmly attached coating of carbon.

Case-hardening is effected by more highly carburetting the surface of soft iron or steel. Objects of soft iron are heated, together with powdered cast-iron turnings, powdered charcoal or potassium ferrocyanide, and thus a superficial coating of more highly carburetted steel is given to them.

The *Harvey process* is of a similar character, and is now applied to armour plates in order to give them a hard surface capable of offering resistance to a modern projectile. This process is carried out by heating the plate of mild steel or nickel steel to about the melting point of cast-iron in contact with carbonaceous material, which is tightly rammed down upon its surface. When

the surface of the plate has absorbed about 1 per cent. of extra carbon the plate is withdrawn from the heating chamber and quenched with cold water.

The following table shows the amount of carbon in the steel employed for the manufacture of various articles.

	Carbon.
Armour plate	0·23–0·75
Boiler plate	0·15
Files	1·48
Gun tubes, Woolwich . . .	0·2–0·4
Rails	0·25–0·35
Cutting tools	1·0–1·5

Special Steels.—Many varieties of steels are now made for special purposes, which contain larger amounts of various elements than are usually present in appreciable quantity. Manganese steel is used in the construction of dynamos, on account of its non-magnetic properties. Nickel steel (p. 1047) is employed for armour plates; chromium steel for projectiles; tungsten steel for tools, &c.

550 *Recalescence of Steel.*—When steel is allowed to cool from a temperature of about 1000°, it is found as a rule that at three different temperatures the regularity of the cooling is interrupted, an evolution of heat taking place which prolongs the period required for the metal to cool through a given range of temperature. This phenomenon is known as *recalescence*, and the three changes are termed, A_3 (about 850°), A_2 (about 750°), and A_1 (about 650°). They are not, however, equally well marked in all varieties of steel, and, with the exception of the second, the temperatures at which they occur vary with the composition of the steel. The last change (650°) is the most pronounced, and can readily be rendered evident by allowing a heated bar of steel to cool when loaded with a weight just insufficient to bend it when hot. When the iron reaches the temperature of recalescence (650°) it is seen suddenly to bend. The effect of the rise of temperature in the bar can easily be observed in a dark room.

551 *Constitution of Steel.*—Two views are held by different chemists as to the constitution of steel and the cause of hardening and of recalescence. Both agree in regarding the lowest point of recalescence (A_1, 650°) as due to the formation of carbide of iron, Fe_3C (p.1018). All steel which is slowly cooled from above

this temperature contains the greater portion of its carbon in the form of this carbide, whilst steel which is suddenly cooled from a higher temperature scarcely contains any of it.

According to one of the opposing views (Osmond, Roberts-Austen) the other two points, A_2 and A_3, mark the occurrence of allotropic changes in the iron present; the metal being supposed capable of existing in three allotropic forms, as γ-iron above 850°, as β-iron between 850° and 750°, and as α-iron below 750°. When heated steel is suddenly cooled, the γ or β form persists, and the result is a hard and brittle metal; if the temperature be allowed to fall slowly below 750°, the α form is produced and a soft metal results. In the absence of carbon, the β form invariably passes into α-iron, even when suddenly cooled. According to the second view (Arnold, Howe), the recalescence at 850° marks the formation of an intensely hard sub-carbide of iron, $Fe_{24}C$ (p. 1018), which remains unaltered if the metal be suddenly cooled. This carbide is easily decomposed by dilute acids with evolution of hydrocarbons, and it is actually found that when hardened steel is attacked by dilute acids, the greater part of its carbon is given off in this form. If the steel be cooled slowly, the carbide is decomposed with evolution of heat into iron and carbide of iron, Fe_3C, and a soft metal thus produced which leaves the greater part of its carbon behind in the form of Fe_3C when it is acted on by dilute acids. The change A_2 at 750° seems from microscopical evidence to be simply due to the crystallisation of the iron.

Further researches, especially on the properties of pure iron, are required before the question can be settled and much information may be expected from the further application of the microscope to the study of the crystalline condition of steel and iron, which has already yielded valuable results.

COMPOUNDS OF IRON.

Iron and Oxygen.

552 Iron forms three oxides,

Iron monoxide, or ferrous oxide, FeO,

Magnetic oxide of iron, or ferroso-ferric oxide, Fe_3O_4,

Iron sesquioxide, or ferric oxide, Fe_2O_3.

The two latter oxides occur in nature as minerals, and are not only used as ores of iron but are also employed in medicine.

Indeed rust of iron (ferric hydroxide) is said to have been used as a medicine by Esculapius, and Dioscorides also mentions *σκωρία σιδήρου*, probably denoting by that iron-scales, as being a substance similar to rust but possessing less active medicinal properties. Red hæmatite was termed blood-stone, and the same author states that this may be obtained artificially by igniting loadstone. Pliny terms iron-rust or scale *squama ferri*, red-iron ore *hæmatites*, and loadstone *magnes*, and describes the action of the latter upon iron. The reddish-yellow and red oxide of iron is called *crocus martis* by the Latin Geber. The later chemists describe various methods for its preparation, and in 1735 the artificially prepared black oxide was termed *ætheops martis*. For a long time these compounds were only distinguished by their different medicinal action. The supporters of the phlogistic theory considered them to be compounds of iron calx with various proportions of phlogiston. Thus, for instance, Scheele in 1777 states that the precipitate which an alkali produces in a solution of green vitriol when exposed to the air gives rise to crocus martis and that fire-air or oxygen disappears. Hence he concludes that the precipitated calx gives up phlogiston in its conversion into crocus.

Lavoisier distinguished two oxides, æthiops and crocus. Other chemists, like Berthollet, believed that a large number of these oxides existed, and so lately as 1811 the views of chemists on this subject were much divided. Gay-Lussac was the first to point out that in addition to the lower and higher oxide an intermediate compound exists, and this conclusion was confirmed by the investigations of Berzelius.

Ferrous oxide acts as a basic oxide, yielding the readily oxidisable ferrous salts, FeR'', in which the metal is divalent. Ferric oxide also acts as a basic oxide, yielding the ferric salts, FeR''', in which the metal is trivalent, but also has a feeble acidic function, forming with many basic oxides a series of compounds known as the ferrites, $M''OFe_2O_3$. The magnetic oxide does not correspond to any characteristic series of salts, but yields a mixture of ferrous and ferric salts when it is treated with acids. It may be regarded as a ferrous ferrite, $FeO.Fe_2O_3$. Salts termed *ferrates* are also known corresponding to the acidic oxide FeO_3, which has not itself been prepared.

Iron Monoxide, or *Ferrous Oxide*, FeO, is obtained when hydrogen is passed over the sesquioxide heated to 300°, as a black powder, which oxidises with incandescence on exposure,

but loses this property after it is allowed to remain for twelve hours in an atmosphere of hydrogen (Siewert). It is also formed by the action of nitrous oxide on metallic iron at 200°.[1] When ferrous oxalate, FeC_2O_4, is heated from 150° to 160° in absence of air, a mixture of monoxide and metallic iron is formed, as shown by the observation of Liebig that the gas evolved consists of fifty-six parts of carbon monoxide and sixty-eight parts of carbon dioxide. If ferrous oxalate is added to boiling caustic potash the monoxide is obtained as a black velvety powder, which when washed with water in the air takes up oxygen (Böttger).

Ferrous Hydroxide, $Fe(OH)_2$, is formed when a pure ferrous salt is treated with caustic potash or soda freed from air. It is a white powder which when washed with hot water and ether in absence of air, may be preserved in an atmosphere of hydrogen. As, however, it is difficult to obtain perfect absence of air, the ferrous hydroxide is usually obtained as a green pulverulent mass.[2] It crystallises from solution in strong caustic soda in flat green prisms.[3]

Ferrous hydroxide becomes heated on exposure to air, the mass sometimes becoming incandescent with formation of sesquioxide. It also rapidly absorbs carbon dioxide, and dissolves in acids with evolution of heat. The moist hydroxide also absorbs atmospheric oxygen, changing colour first to a dirty green and afterwards to a brown.

Ferrous hydroxide is formed by the action of pure water, containing air in solution, on iron. It dissolves in about 150,000 parts of water forming an alkaline liquid which possesses the peculiar taste of the ferrous salt.

Ferrous hydroxide readily dissolves in acids to form the ferrous salts, which are also produced by the direct action of acids on metallic iron in the absence of oxidising agents, and by the reduction of the corresponding ferric salts. The anhydrous ferrous salts of colourless acids are usually colourless, but the corresponding hydrated salts possess a light greenish blue tint. The soluble salts possess a sweet, astringent ink-like taste. Their solutions readily absorb oxygen with formation of a ferric salt, part of which is precipitated in the form of basic salt when there is no excess of acid present. In

[1] Sabatier and Senderens, *Compt. Rend.* 1892, **114**, 1429.
[2] G. Schmidt, *Annalen*, 1840, **36**, 101.
[3] Schulten, *Compt. Rend.* 1889, **109**, 266.

consequence of the ease with which they pass into a higher state of oxidation, the ferrous salts act as powerful reducing agents, and are largely employed for this purpose, both in the laboratory and in the workshop.

Magnetic Oxide of Iron, Ferroso-Ferric Oxide, or *Triferric Tetroxide,* Fe_3O_4, occurs in large masses as the mineral magnetite. It crystallises in octohedra, dodecahedra, and other combinations of the regular system. It has an iron-black colour, and a more or less strong metallic lustre. It frequently occurs in granular or amorphous masses, and is also found in marshes as an earthy mass known as ochreous iron ore (or in German *eisenmulm*). The pure crystallised mineral has a specific gravity of 5·18, whilst that of the granular and earthy material varies considerably, inasmuch as it contains magnesia, lime, titanic oxide, and also often contains the iron in a more highly oxidised condition.

The interesting observation that this ore has the power of attracting iron, and that by contact with it iron attains the same polar magnetic properties, was early made. According to some the name is derived from a certain Magnes who was the first to observe this property, whilst according to others the name is derived from Magnesia, a town in Lydia also called Heraclea, where the mineral was first found. The latter explanation would seem to be the more probable, inasmuch as Plato and Theophrastus term magnetite the Heraclean stone. Ferroso-ferric oxide does not always possess the magnetic properties exhibited by loadstone, although attracted by the magnet.

When iron is heated to redness in the air it becomes coated with an iron scale. This is a mixture or a compound of the monoxide and sesquioxide in varying proportions. The inner layer which is blackish-grey, porous, brittle, and attracted by the magnet, has the composition $6FeO + Fe_2O_3$, and is not magnetic. The outer layer contains a larger quantity of ferric oxide, is of a reddish colour, and is more strongly attracted by the magnet than the inner portion. When iron is quickly burnt in oxygen or in the oxy-hydrogen blow-pipe, the oxide which is formed varies in composition according to the conditions of the experiment, although it approaches the composition of the magnetic oxide, and the occurrence of this oxide has also been observed in smelting operations.

Magnetic oxide is also obtained when steam or carbon dioxide

is passed over red-hot iron, but, on the other hand, when the oxides of iron are heated in a current of hydrogen or of carbon monoxide, they are reduced to metal. When the black oxide is dissolved in hydrochloric acid, or when a mixture in the right proportions of a ferrous and ferric salt is dissolved, and caustic alkali added to the solution, a black precipitate is obtained which dries to a brownish-black brittle mass giving a dark-brown powder which is unalterable in the air. This hydroxide contains about 7 per cent. of water, and corresponds to the formula $Fe(OH)_2.Fe_2O_3$. It is attracted by the magnet and may in this way be separated from any admixed sesquioxide.

553 *Iron Sesquioxide,* or *Ferric Oxide,* Fe_2O_3, is one of the most important ores of iron, occurring as red hæmatite, and as specular iron, crystallising in rhombohedra and scalenohedra, possessing a steel-grey colour. It also occurs under the name of micaceous iron in thin red translucent scales. This mineral is found in large quantity and in splendid crystals in the Island of Elba, of which Virgil[1] says: "Insula inexhaustis chalybdum generosa metallis." The crystals have a specific gravity of 5·19 to 5·25.

The mineral martite is also a pure ferric oxide which crystallises in the same form as magnetic oxide, and is probably a pseudomorph of this mineral. Other more or less pure forms of ferric oxide are red- and yellow-ochre and bole.

Ferric oxide can be prepared artificially in various ways. It is formed by igniting the hydroxide or any ferric salt containing a volatile acid, as a steel-grey crystalline powder, which like all other kinds of sesquioxide of iron, gives a brownish-red powder when finely triturated, and has a specific gravity of 5·17. It may be obtained in small crystals by the action of the vapour of ferric chloride on heated lime (Daubrée), or by fusing ferric oxide and borax together and treating the cooled mass with hot dilute hydrochloric acid; also by passing a slow steady stream of hydrochloric acid over the strongly ignited oxide (Deville). Artificial micaceous iron is prepared by heating a solution of ferrous sulphate and copper sulphate together for ten hours at a temperature of 210° (Wibel). Ferric oxide has also been observed in the crystalline state as a product in smelting operations, whilst crystals having the form of specular iron, have been found in iron-rust from a building some 700 to

[1] *Æn.* x. 173—4.

800 years old. The ignited as well as the natural ferric oxide dissolves only slowly in acids, the best solvent being a boiling mixture of eight parts of sulphuric acid and three parts of water. Ordinary ferric oxide is only very slightly paramagnetic, and is not attracted by a small horse-shoe magnet. It has, however, been obtained in a more strongly magnetic form by the oxidation of ferrous hydroxide,[1] and Liversedge has described specimens of rust, which, although free from metallic iron and from ferrous oxide, are strongly magnetic.[2] When it is heated in the electric furnace it melts and forms the magnetic oxide,[3] which is also produced when it is heated in the oxyhydrogen flame.[4]

In addition to its use as an iron ore, ferric oxide is of service in a variety of other ways. Thus, the residue left in the process of distilling fuming sulphuric acid from green vitriol (vol. i., p. 402), termed *colcothar* or *caput mortuum vitrioli*, is used largely as an oil-paint and also as a polishing powder; the least calcined portions, which are of a scarlet colour, are used as jewellers' rouge, whilst the more calcined portions which have a bluish tint are termed *crocus*, and are employed for polishing brass or steel.

Ferric Hydroxide, $Fe(OH)_3$, is prepared by precipitating a moderately dilute solution of ferric chloride with an excess of ammonia in the cold, a voluminous brown precipitate of the hydroxide being thrown down. The composition of this substance does not undergo change on washing, or on slightly heating, when it forms a dry amorphous granular powder. If the water containing the precipitate be allowed to freeze, a microscopic crystalline powder is formed, and this substance corresponds in composition to the minerals brown-hæmatite and limonite, viz., $Fe_2O_3+2Fe(OH)_3$. This hydroxide also exists in nature as ochre, likewise as the deposit of chalybeate waters, the colouring matter of yellow sandstone, &c. Iron-rust has the same composition, as well as the precipitate which is obtained when a ferric salt is precipitated hot, and the precipitate dried over sulphuric acid. When the hydrated oxide is heated, its composition varies gradually with the temperature, the last portions of water being driven off at 500°.[5]

[1] Malaguti, *Compt. Rend.* 1862, **55**, 350. [2] *Chemical News.*
[3] Moissan, *Compt. Rend.* 1892, **115**, 1034.
[4] Read, *Journ. Chem. Soc.* 1894, **1**, 314.
[5] Carnelley and Walker, *Journ. Chem. Soc.* 1888, i. 89.

When allowed to remain for a long time in contact with water the hydroxide becomes crystalline, losing thereby the half of its water. The red amorphous compound, $Fe_2O_4H_2 = Fe_2O_3 + H_2O$, is often formed under similar circumstances, and also when a boiling solution of green vitriol is mixed with sodium carbonate and sodium hypochlorite. It occurs as the mineral göthite, having a specific gravity of 4·34. The precipitated ferric hydroxide when heated for some days at a temperature of 100°, forms a scarlet powder $Fe_4O_7H_2 = 2Fe_2O_3 + H_2O$, having a specific gravity of 4·45, and dissolving with difficulty in nitric acid although more readily in hydrochloric acid. This occurs in nature as the mineral turgite. In addition to these, other hydroxides are known; these are obtained by precipitating the ferric salts under various conditions.

Iron only rusts in the presence of oxygen and liquid water containing either carbonic acid, some other volatile acid or a metallic salt in solution. In the presence of carbonic acid ferrous bicarbonate appears to be first formed with evolution of hydrogen, which afterwards decomposes in presence of the oxygen, forming a hydrated ferric oxide and regenerating the carbonic acid.

Soluble Ferric Hydroxide.—When freshly precipitated ferric hydroxide is added to a solution of ferric chloride, it dissolves to form a basic chloride with production of a dark-red liquid. This may also be obtained by adding ammonium carbonate to a solution of ferric chloride, until the precipitate which is first formed no longer redissolves. If a solution of this kind containing about 5 per cent. of solid constituents be allowed to dialyse for a long time, a dark-red fluorescent liquid remains which contains only 1·5 parts of hydrochloric acid to 98·5 of ferric oxide. On standing for some weeks this solution gelatinises, a ferric hydroxide separating out which is readily soluble in cold acids. When the solution is filtered through a porous cell, the whole of the iron and hydrochloric acid remains behind.[1]

The same compound may be obtained by the dialysis of ferric acetate, and a liquid thus obtained which only contains six parts of acetic acid to ninety-four parts of oxide of iron. Hydrochloric acid, nitric acid, sugar, and alcohol, do not produce gelatinisation in such a solution, although traces of alkalis and many acids do produce this effect. This soluble hydroxide is used as a medicine under the name of *Liquor Ferri Dialysati.*

[1] Picton and Linder, *Journ. Chem. Soc.* 1892, i. 152.

Soluble Meta-ferric Hydroxide, $Fe_2O_4H_2$.—This substance was discovered by Péan de St. Gilles.[1] It is formed when solutions of certain iron salts containing monobasic acids are heated for a length of time, and is precipitated from these solutions by the addition of a small trace of sulphuric acid as a brown ochreous powder. It is also obtained by heating a solution of basic ferric nitrate for three days to 100°. On addition of a few drops of hydrochloric acid the hydroxide is precipitated, and this may be dried on a porous plate where it remains in the form of black scales which dissolve in water, yielding a tasteless red liquid.[2] The same body may be obtained by heating dilute ferric chloride solution and adding common salt; the precipitate which is then thrown down dissolves in pure water, to form a reddish-yellow solution, appearing transparent by transmitted, but opalescent by reflected light.[3]

Meta-ferric hydroxide is insoluble in concentrated, but dissolves in dilute acids, forming solutions which exhibit the same optical properties as that of the hydroxide itself.

Ferric hydroxide forms a compound with sugar, which is soluble in water. This fact is of great importance to the sugar refiners, as this compound destroys the crystallising power of sugar, and therefore increases the quantity of molasses formed. Hence raw sugar ought not to be brought into contact with iron, and the "char" employed for the decolorisation of the sugar should be as free as possible from the compounds of this metal.

554 Ferric oxide combines with several basic monoxides to form compounds known as ferrites, corresponding to ferroso-ferric oxide, all of which resemble this in being magnetic.

Calcium Ferrite, $Fe_2O_3.CaO$.[4]—This compound is obtained when an intimate mixture of 190 parts of sesquioxide of iron and 66·5 parts of lime is heated to whiteness in a platinum vessel for several hours. It forms a brittle mass of interlaced acicular crystals exceeding an inch in length, having a dark metallic lustre. Its specific gravity is 4·693; it yields a brown powder, which is also obtained by precipitating a solution of ferric chloride, as nearly neutral as possible, with lime-water or saccharosate of lime, and igniting the precipitate.

[1] *Ann. Chim. Phys.* 1856 [3], **46**, 47.
[2] Scheurer-Kestner, *Ann. Chim. Phys.* 1859 [3], **57**, 23.
[3] Debray, *Compt. Rend.* 1869, **68**, 913.
[4] Percy, *Phil. Mag.* 1873 [4], **45**, 455.

Magnesium Ferrite, $Fe_2O_3.MgO$, occurs in nature crystallising in black octohedra as magnoferrite, and is artificially obtained by the ignition of a mixture of the two oxides in a current of hydrochloric acid, or by the precipitation of a mixture of ferric chloride and magnesium chloride with a quantity of caustic soda insufficient to throw down the whole. Many analogous compounds can be prepared in a similar way.[1]

Zinc Ferrite, $Fe_2O_3.ZnO$, was obtained by Ebelmen, crystallised in black octohedra, by strongly igniting both oxides together with boron trioxide. The mineral franklinite has a similar composition.

Ferric hydroxide dissolves readily in acids to form the ferric salts, which may also be obtained by the action of oxidising agents on the corresponding ferrous salts. In the anhydrous state they are generally colourless; in the hydrated state they are yellow or brown. The soluble ferric salts possess a peculiar astringent taste, and they pass readily by reduction into the corresponding ferrous compounds.

555 *Ferric Acid*, H_2FeO_4.—This compound, like manganic acid, is not known in the free state. In the year 1702 Stahl noticed that when iron is fused with saltpetre and the solid mass lixiviated, or when a solution of iron in nitric acid is added to concentrated potash-ley, an amethyst or purple-red coloured solution is formed. Exactly a century afterwards Eckeberg published his memoir on "Yttria," in which he states that when gadolinite is fused with potash and the fused mass extracted with water, the solution possesses a dark purple-red colour, due to iron and not to manganese. The potassium ferrate formed under these circumstances was more carefully examined by Fremy.[2] It is prepared by igniting iron-filings or iron oxide with saltpetre or caustic potash, or a mixture of both. The formation of the compound may be readily shown by heating a mixture of one part of powdered iron with two parts of saltpetre in a small glass bulb, over a Bunsen burner. After a few minutes the mass becomes red-hot, and when cold the residue is dissolved in water.[3] The purple solution is also obtained by passing chlorine through a strong solution of caustic potash, in which ferric hydroxide is suspended (Fremy), and by passing a current of electricity through a solution of caustic potash by means of a positive pole of cast-iron, this solution after a time

[1] List, *Ber.* 1878, **11**, 1512. [2] *Journ. Pharm.* **27**, 97.
[3] Hofmann, *Ber.* 1869, **2**, 239.

appearing almost black.[1] If more caustic potash be added to the concentrated and almost opaque solution a reddish-brown precipitate of potassium ferrate is formed. This may be dried on a porous plate, and then can be preserved in a sealed tube. It is a very unstable substance; its solution becomes colourless on standing, and on heating ferric hydroxide separates out with evolution of oxygen. Nitric acid and dilute sulphuric acid produce a similar result, a ferric salt being formed, whilst hydrochloric acid decomposes it with evolution of chlorine.

Barium Ferrate, $BaFeO_4 + H_2O$, is obtained in the form of a dark red powder by precipitating the potassium salt with barium chloride. It is tolerably stable, and is soluble in acetic acid, yielding a red solution. When gently heated it becomes green, and when strongly heated it decomposes with evolution of oxygen and loss of water.

Iron and Hydrogen.

556 By acting upon anhydrous ferrous iodide with zinc-ethyl $(C_2H_5)_2Zn$, in presence of ether, Carius and Wanklyn obtained, together with zinc iodide, a mixture of gases consisting of ethylene C_2H_4; ethane, C_2H_6; butane, C_4H_{10}; and hydrogen. The residue after washing with ether yields a metallic powder resembling iron which does not undergo any alteration in dry air, but evolves hydrogen on heating, and is decomposed by water with evolution of hydrogen, leaving a residue of metallic iron and ferrous oxide. Hence it would appear that a compound of iron and hydrogen exists which has probably the composition FeH_2. Hydrogen is occluded by electrolytic iron which absorbs 9—19 times its volume of this gas.

Iron and the Halogens.

557 *Ferrous Fluoride*, FeF_2, is obtained in colourless or greenish prisms, $FeF_2 + 8H_2O$, by dissolving iron in hydrofluoric acid and evaporating; these crystals decompose when gently heated, leaving the anhydrous salt, which is formed when iron or ferric chloride is heated in dry hydrofluoric acid gas, and crystallises in colourless rhombic prisms.

[1] Poggendorff, *Pogg. Ann.* 1841, **54**, 373.

Ferric Fluoride, FeF_3, is obtained by dissolving the hydroxide in hydrofluoric acid, colourless crystals of $2FeF_3+9H_2O$ separating out from the colourless solution on evaporation. The anhydrous salt may also be prepared in a similar way to the ferrous compound. It does not fuse even at 1000°, and forms ferric oxide when heated in the air.[1]

Several double salts with the alkali fluorides are known.

Ferrous Chloride, $FeCl_2$, is obtained by passing chlorine over iron filings (Thénard), but as a small quantity of ferric chloride is generally formed, even when an excess of iron is present, it is preferable to pass hydrochloric acid over iron filings, or iron wire heated to redness (Wöhler and Liebig), or to reduce ferric chloride by heating it in a stream of pure hydrogen. Ferrous chloride is deposited in colourless shining scales, which, according to Sénarmont, are six-sided. It has a specific gravity of 2·528 (Filhol), and is very deliquescent, dissolving readily in water and alcohol. It fuses at a red-heat, and volatilises at a yellow heat, when its vapour has a specific gravity of 6·38—6·67,[2] whilst at 1300—1500° it acquires the normal value of 4·3.[3]

When heated in the air it oxidises to ferric chloride, which volatilises, ferric oxide remaining behind:

$$12FeCl_2+3O_2=8FeCl_3+2Fe_2O_3.$$

When heated in a current of steam magnetic oxide is formed:

$$3FeCl_2+4H_2O=Fe_3O_4+6HCl+H_2.$$

When iron is dissolved in hydrochloric acid, and the solution concentrated in absence of air, bluish transparent monosymmetric crystals of $FeCl_2+4H_2O$ are obtained; these have a specific gravity of 1·93, deliquesce and become greenish coloured on exposure to the air, but effloresce at ordinary temperatures when kept over oil of vitriol; if a solution of this salt be evaporated with sal-ammoniac in absence of air, and the solid mass heated in a flask until the whole of the sal-ammoniac is volatilised, a residue of anhydrous ferrous chloride is left. Like other soluble ferrous salts, the solution of ferrous chloride absorbs nitric oxide, forming a dark greenish-brown solution, containing the compound $FeCl_2.NO$. This substance is very unstable, losing the whole of its nitric oxide on warming, or when placed

[1] Poulene, *Compt. Rend.* 1892, **115**, 941.
[2] V. Meyer, *Ber.* 1884, **17**, 1335.
[3] Nilson and Pettersson, *Journ. Chem. Soc.* 1888, i. 827.

in a vacuum. The anhydrous chloride readily absorbs ammonia, swelling up to form a white powder (Faraday), having the composition $FeCl_2.6NH_3$ (Rostadius).

Ferroso-ferric Chloride, $Fe_3Cl_8+18H_2O$. Magnetic oxide of iron dissolves readily in concentrated hydrochloric acid, forming a yellow liquid, which on concentration over sulphuric acid deposits the above salt in opaque yellow deliquescent crystalline crusts.

Ferric Chloride, $FeCl_3$. The aqueous solution of this salt was known to Glauber under the name of *oleum martis*. He obtained it in the dry state by dissolving iron in hydrochloric acid and evaporating the solution in a flask: "*In fundo* there remains a blood-red *massa*, which is as hot to the tongue as fire. It must be well kept from the air, otherwise it liquefies to a yellow *oleum*."

Anhydrous ferric chloride is obtained by heating iron wire in a current of dry chlorine gas at a moderate red-heat, when rapid combination with ignition takes place, ferric chloride being deposited. It is also produced when hydrochloric acid is passed over heated amorphous ferric oxide, and is not infrequently found in the craters of volcanoes.

Ferric chloride forms iron-black iridescent plates or sometimes large hexagonal tables, which exhibit a red colour by transmitted and a green metallic lustre by reflected light. It is very deliquescent and easily soluble in water, alcohol, and ether. It easily volatilises even at 448°, and its vapour-density at that temperature is less than is required by the formula Fe_2Cl_6. Hence its molecular formula is $FeCl_3$.[1] (See p. 33). At higher temperatures it decomposes into ferrous chloride and chlorine. When dissolved in boiling alcohol or ether it appears to have a molecular weight corresponding to the formula $FeCl_3$.[2]

Ferric chloride forms with ammonia the compound $FeCl_3+4NH_3$, which does not differ in appearance from ferric chloride itself. It also absorbs nitrosyl chloride, yielding a dark-coloured deliquescent compound, $FeCl_3+NOCl$, and unites with nitric oxide at the ordinary temperature to form several unstable compounds, whilst at higher temperatures it is reduced by the gas to ferrous chloride.[3] When heated in a current of steam

[1] Grünewald and V. Meyer, *Ber.* 1888, **21**, 687. Compare Friedel and Craft, *Compt. Rend.* 1888, **107**, 301.

[2] Muller, *Compt. Rend.* 1894, **118**, 641.

[3] Besson, *Compt. Rend.* 1889, **108**, 1012; Thomas, *Compt. Rend.* 1895, **120**, 447; **121**, 128.

it is decomposed into ferric oxide and hydrochloric acid, and when heated in oxygen, chlorine is evolved, ferric oxide remaining.

For the purpose of obtaining a solution of ferric chloride, the hydroxide may be dissolved in hydrochloric acid and the liquid evaporated in order to drive off excess of acid, or a solution of ferrous chloride may be heated with the requisite quantity of hydrochloric acid and the heated solution oxidised by addition of nitric acid. The solution of ferric chloride is, however, best prepared by dissolving iron wire in hydrochloric acid, as described under the preparation of ferrous chloride, and then passing chlorine into this solution until, after standing for some time, it smells strongly of the gas. The excess of chlorine is then displaced by passing a current of carbon dioxide through the warm liquid. A concentrated solution of ferric chloride has a dark brown colour and an oily consistency. On dilution it becomes limpid, and has a slightly yellow colour. Its specific gravity at 17° is as follows (Fremy):—

Percentage of $FeCl_3$.	Specific Gravity.	Percentage of $FeCl_3$.	Specific Gravity.
1	1·0073	40	1·3622
10	1·0734	50	1·4867
20	1·1542	60	1·6317
30	1·2658		

Four different hydrates of ferric chloride have been described by Roozeboom,[1] $FeCl_3+6H_2O$, melting at 37°; $2FeCl_3+7H_2O$, melting at 32·5°; $2FeCl_3+5H_2O$, melting at 56°; and $FeCl_3+2H_2O$, melting at 73·5°. Solutions which contain more iron than corresponds to the formula $FeCl_3+2H_2O$ deposit the anhydrous salt when evaporated above the temperature of 66°. A deliquescent compound, $FeCl_3.HCl+2H_2O$, is formed by the action of hydrochloric acid on the pentahydrate, whilst similar compounds with $4H_2O$ and $6H_2O$ are also known.[2] The aqueous solution of the normal chloride is decomposed on heating, the more easily the more dilute the solution is, an insoluble oxychloride or soluble ferric hydroxide being produced according to the concentration of the liquid.

The solutions of ferrous and ferric chlorides have long been

[1] *Zeit. Phys. Chem.* 1892, **10**, 477.

[2] Sabatier, *Bull. Soc. Chim.* 1881 (2), **36**, 197; Roozeboom and Schreinemaker, *Zeit. Phys. Chem.* 1894, **15**, 588.

used in medicine. An alcoholic solution of ferric chloride was formerly employed as a quack medicine of repute, known by the name of Lamotte's golden drops. This solution loses its colour when exposed to light, ferrous chloride being formed, the latter compound separating, when the solution is not too dilute, in fine green crystals, $FeCl_2+2H_2O$.

Ferric chloride forms garnet-red-coloured crystalline double salts with the chlorides of the metals of the magnesium group and of the alkali metals, such as $FeCl_3+MgCl_2+H_2O$, $FeCl_3+2KCl+H_2O$, and $FeCl_3+2NH_4Cl+H_2O$. These are decomposed by water, and a mixture of the last salt with an excess of sal-ammoniac is termed iron-sal-ammoniac; it was formerly obtained by sublimation of a mixture of iron oxide and ammonium chloride, and is mentioned by "Basil Valentine." Sal-ammoniac crystallises in yellow or bright red transparent regular crystals from a dilute solution of ferric chloride; these contain a varying amount of iron, and rapidly absorb moisture from the air.

Iron Oxychlorides.—These compounds are formed in various ways. Some are soluble, whilst others are insoluble in water. When freshly precipitated ferric hydroxide is added to a solution of ferric chloride, it dissolves in considerable quantity, and a dark-red liquid is obtained, which, to one molecule of chloride, may contain twenty or more molecules of oxide, and this on dialysis furnishes Graham's soluble oxide. These solutions may be diluted or warmed without any precipitation of ferric oxide. Many acids and salts, however, precipitate either ferric hydroxide or a basic chloride from these solutions, which latter is again soluble in water. If ferric chloride be incompletely precipitated with alkalis, a precipitate is also obtained which is soluble in water when it does not contain more oxide than is indicated by the formula, $FeCl_3+5Fe(OH)_3$.

Insoluble basic ferric chlorides are formed, in the first place by the oxidation of ferrous chloride in the air; secondly, by roasting iron in the presence of hydrochloric acid or a chloride; and, thirdly, by boiling a solution of ferric chloride for some time. The composition and colour of these salts vary according to the mode of preparation. They are generally sparingly soluble in hydrochloric acid.

Ferrous Bromide, $FeBr_2$.—When bromine vapour is passed over iron heated to a dull redness, heat is evolved, and a yellowish crystalline deposit of ferrous bromide is formed (Liebig). An

aqueous solution of ferrous bromide can easily be obtained by dissolving iron in hydrobromic acid, and on crystallising bluish-green rhombic tables are deposited, having the composition $FeBr_2+6H_2O$ (Löwig).

Ferric Bromide, $FeBr_3$.—This is obtained in the form of dark-red crystals by heating iron in an excess of bromine vapour. When heated in absence of air it fuses, and a part may be sublimed without decomposition, another portion, however, being decomposed into ferrous bromide and free bromine. The bromide deliquesces on exposure to air, and the solution, which may be simply obtained by dissolving the hydroxide in hydrobromic acid, decomposes on evaporation, with formation of insoluble basic bromides. Like the chloride, the solution of the bromide dissolves ferric hydroxide readily with formation of soluble oxybromides. It forms double salts with certain of the alkali bromides.

An unstable ferric chlorobromide, $FeCl_2Br$, is formed by the direct union of ferrous chloride and bromine.[1]

Ferrous Iodide, FeI_2, is obtained by triturating iodine with a slight excess of iron filings, or by heating the latter in a covered porcelain crucible to redness, small quantities of iodine being gradually added; as soon as the whole mass becomes red-hot, a large quantity of iodine is thrown in, and the crucible heated until iodine vapour ceases to be given off. On allowing the crucible to cool it is found that a further evolution of iodine vapour takes place, probably due to the fact that the fused mass contains an unstable ferric iodide, which decomposes on cooling. The solid residue found is a grey lamino-crystalline mass, which melts at 177°.[2] If a mixture of iodine and iron filings be warmed with water, these elements combine with evolution of heat, and a colourless aqueous solution of ferrous iodide is obtained, which on exposure to the air readily oxidises with separation of iodine. This decomposition is prevented by the addition of sugar. It crystallises with $5H_2O$.

Ferric Iodide does not appear to exist.

Ferrous Perchlorate, $Fe(ClO_4)_2+6H_2O$, is the only iron salt of the oxyacids of chlorine which is stable in the solid state. It is obtained by the double decomposition of ferrous sulphate and barium perchlorate (Serullas), or by dissolving iron in dilute

[1] Lenormand, *Compt. Rend.* 1893, **116**, 820.
[2] Carius and Wanklyn, *Annalen*, 1861, **120**, 69.

perchloric acid (Roscoe). It forms very light green deliquescent crystals, which at 100° give off water, and decompose at a higher temperature.

Iron and Sulphur.

558 *Iron Monosulphide*, or *Ferrous Sulphide*, FeS, occurs as triolite in small quantities in many meteorites, and is easily formed by the direct union of the elements. Iron wire burns in sulphur vapour with a bright light, and a roll of sulphur penetrates red-hot wrought-iron and steel, but not cast-iron, with formation of the molten sulphide.[1] In order to prepare this substance a mixture of three parts of iron filings and two parts of sulphur is thrown gradually into a red-hot crucible. In this way a porous black mass is obtained which melts at a higher temperature, with separation of sulphur if any higher sulphides have been formed, but as a rule the artificial sulphide contains an excess of iron, and this is got rid of by heating with an excess of sulphur. For the preparation of the monosulphide Berzelius recommends the process proposed by Gahn, namely, to stir a white-hot rod of iron in molten sulphur. The sulphide which is formed fuses and falls to the bottom of the crucible. The operation is continued as long as any free sulphur remains. Pure monosulphide of iron is a yellowish crystalline mass having a metallic lustre, and sometimes crystallising in hexagonal prisms. It has a specific gravity of 4·69, is not magnetic, and does not lose sulphur when ignited to an atmosphere of hydrogen, or when heated in absence of air in whiteness. It is readily decomposed by hydrochloric and dilute sulphuric acids with formation of sulphuretted hydrogen, and is used as a source of this gas in the laboratory. When heated in the air it oxidises, being converted partly into ferrous sulphate, whilst at a high temperature sulphur dioxide and ferric oxide are formed. Ammonium sulphide precipitates sulphide of iron from solutions of ferrous salts as a black amorphous hydrated precipitate, whilst the same re-agent throws down from ferric salts a mixture of monosulphide and sulphur:

$$2FeCl_3 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl.$$

If seven parts of iron filings and four parts of sulphur be rubbed up to a paste with water a black sulphide is also produced

[1] Evain, *Ann. Chim. Phys.* **25**, 106.

with evolution of heat. In this form it oxidises very quickly in the air with increase of temperature which, when the mixture is in large quantity, may rise to incandescence. Hence, according to Lemery, artificial volcanoes may be formed if several pounds of the above mixture be buried in the earth. The black amorphous sulphide is also formed by the reduction of ferric oxide or its salts in presence of sulphates and decomposing organic matter. This is the cause of the black deposit found in drains as well as in the excrement when iron is used as a medicine.

Iron Sesquisulphide, or *Ferric Sulphide*, Fe_2S_3, does not occur pure in the mineral kingdom, but probably forms a constituent of magnetic pyrites and copper pyrites. It is obtained by gently heating sulphur and iron together as well as by the action of sulphuretted hydrogen on ferric oxide at a temperature not above 100°. The sulphide obtained at a red-heat forms a yellow non-magnetic mass which has a specific gravity of 4·4 and is decomposed by dilute hydrochloric acid into sulphuretted hydrogen, ferrous sulphate, and iron disulphide. Iron sesquisulphide forms compounds with the other sulphides.[1]

Potassium Ferric Sulphide, $K_2Fe_2S_4$, is obtained when iron filings, sulphur, and potassium carbonate are heated together and the residue extracted with water. Purple-coloured glistening needle-shaped crystals are thus obtained which have a specific gravity of 2·863 and burn when heated in the air, but when ignited in a current of hydrogen are converted without change of form into the black compound $K_2Fe_2S_3$.

Sodium Ferric Sulphide, $Na_2Fe_2S_4+4H_2O$, is obtained in a similar way and forms brown microscopic needles.

Silver Ferric Sulphide, $Ag_2Fe_2S_4$, is a dark brownish-black crystalline powder obtained by the action of silver nitrate solution on the potassium compound. It is decomposed by hydrochloric acid with evolution of sulphuretted hydrogen.

Cuprous Ferric Sulphide, Cu_2S,Fe_2S_3, occurs as the mineral copper pyrites.

Magnetic pyrites may be regarded as a compound of the mono- and sesqui sulphides. Its composition varies between $5FeS+Fe_2S_3$ and $6FeS+Fe_2S_3$. It crystallises in hexagonal plates, usually, however, occurring in the massive state, having a brownish-yellow or brassy colour, and is attracted by the magnet, sometimes being itself magnetic. Its specific gravity varies from 4·4 to 4·7, and it frequently contains as much as

[1] Schneider, *Pogg. Ann.* 1869, **136**, 460; Preis, *J. pr. Chem.* 1869, **107**, 10.

5·5 per cent. of nickel, the latter metal being obtained in America from this source in considerable quantities.

Iron Disulphide, FeS_2, occurs very widely distributed as iron pyrites. This mineral was known in early times, but was not distinguished from copper pyrites, both being known under the name of πυρίτης. Agricola considered these as two varieties of the same mineral.

Iron pyrites occurs in all geological formations, and usually crystallises in cubes or pentagonal dodecahedra, but also occurs in many other forms and combinations of the regular system, no less than sixty-nine different forms having been described. It is frequently found in spherical, botryoidal, or stalactytic masses, being formed by the action of organic matter on water which contains iron in solution in the form of sulphate. Hence it is frequently found in peat and in crystalline masses often possessing the form of the original organic matter such as wood, roots, &c. It is likewise found in chalk cliffs, in similar concretionary forms. In the pure state iron disulphide has a brass-yellow colour, and a specific gravity of 5·185. It is very hard, giving sparks when struck with steel, for which purpose it was formerly employed. Iron disulphide also occurs as radiated pyrites and marcasite, forming bright brass-coloured rhombic crystals having a specific gravity of 4·68 to 4·85. This is also widely diffused, occurring in various forms, especially in lignite beds. Iron disulphide may be obtained artificially by gently heating the monosulphide with sulphur, or by passing sulphuretted hydrogen over the oxides or chlorides of iron heated to redness. When an intimate mixture of ferric oxide, sulphur, and sal-ammoniac is heated slowly above the temperature at which the latter compound volatilises, the disulphide is obtained in small brass-yellow octohedra and cubes (Wöhler). Crystalline pyrites is also formed when carbon bisulphide vapour acts upon heated ferric oxide (Schlagdenhauffen), and when ferric chloride is heated with phosphorus pentasulphide.[1] Iron disulphide is not magnetic and is not attacked by dilute acids or sulphuric acid, but readily dissolves in nitric acid with separation of sulphur.

Iron Subsulphide, Fe_4S_3, is formed when iron is heated in the vapour of carbon bisulphide as a crystalline mass of specific gravity 6·957. It dissolves in dilute acids with evolution of hydrogen and sulphuretted hydrogen.[2]

[1] Glatzel, *Ber.* 1890, **23**, 37.

[2] Gautier and Hallopeau, *Compt. Rend.* 1889, **108**, 806.

Ferrous Sulphite, $FeSO_3$. When iron is dissolved in aqueous sulphurous acid in absence of air, no gas is evolved, and the solution contains ferrous sulphite and ferrous thiosulphate:

$$2Fe+3H_2SO_3=FeSO_3+FeS_2O_3+3H_2O.$$

The latter salt is a very soluble one; the first, however, is only slightly soluble, so that after a short time it is deposited in colourless or greenish crystals. When freshly precipitated ferric hydroxide is dissolved in sulphurous acid, a red solution is obtained, which quickly becomes decolorised with formation of ferrous sulphite, whilst, on the other hand, a solution of ferrous sulphide becomes red on exposure to the air.[1]

559 *Ferrous Sulphate*, or *Green Vitriol*, $FeSO_4+7H_2O$, was probably used by Geber. Agricola in his discourse *De re Metallica* mentions two kinds of pyrites. The one, such as coal-brasses, decomposes spontaneously and yields a vitriol; whilst the other, as the ordinary Mason's pyrites, does so only when it is roasted. Its preparation by dissolving iron in sulphuric acid was described by "Basil Valentine" in his *Treatise on Natural and Supernatural Things:* "Take oleum vitrioli; dissolve therein *mars*, and prepare a vitriol from it." In his last volume he describes the method for preparing sulphide of iron and for obtaining from it vitriol: "*Limaturam ferri* and *sulphur ana* calcined in a potter's furnace until it becomes tinted purple; then pour upon this distilled water, when a fine green liquid is formed. Draw this off *ad tertias*, allow it to deposit, and thus obtain an artificial vitriol." Green vitriol occurs as the mineral melanterite, either crystalline or in fibrous stalactitic forms, but generally massive and pulverulent. It is usually derived from the decomposition of pyrites or marcasite. Ferrous sulphate is likewise frequently found in solution in drainage water from mines, and it is manufactured on a large scale from this source. Large quantities of green vitriol (about 100 tons per week) are manufactured in South Lancashire from the pyrites occurring in the coal-measures. These are piled up in heaps and exposed to the atmosphere. The soluble ferrous sulphate, together with the excess of sulphuric acid formed, runs into underground tanks, where the excess of acid is removed by means of scrap iron. On evaporating the liquor large crystals of ferrous sulphate are obtained. Ferrous sulphate is also formed as a bye-product in the

[1] See also Seubert and Elten, *Zeit. anorg. Chem.* 1893, **4**, 44.

manufacture of copper sulphate or blue vitriol (p. 335). The commercial salt not unfrequently contains traces of copper sulphate, and this may be detected and separated, as was pointed out so long ago as 1683 by Vigani, by leaving the solution in contact with metallic iron until the whole of the copper is precipitated. Another common impurity is ferric sulphate; this may be removed by recrystallisation, but zinc sulphate, manganese sulphate, and other salts cannot thus be got rid of. Hence when chemically pure ferrous sulphate is needed, it is best to treat an excess of iron wire with dilute sulphuric acid. When the evolution of hydrogen has ceased, the liquid is boiled together with the undissolved portion of the wire, filtered and evaporated to crystallisation.

Ferrous sulphate forms well-defined monosymmetric crystals (Fig. 179), having a specific gravity of 1·889° at 4° (Joule and

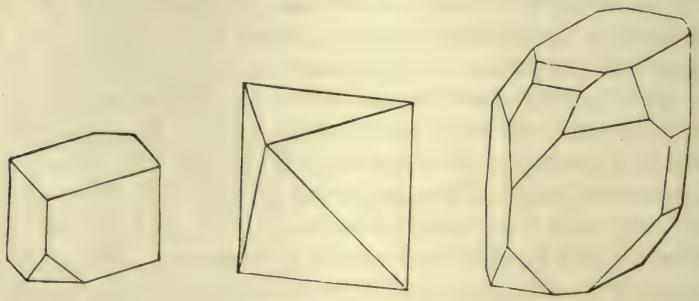


Fig. 179.

Playfair). One hundred parts of water dissolve, according to Brandes and Firnhaber, the following:—

At	10°	15°	33°	60°	90°	100°
$FeSO_4+7H_2O$ . .	61	70	151	263	370	333

Ferrous sulphate is dimorphous, often crystallising in rhombic prisms, which are isomorphous with zinc sulphate. These are easily obtained when a crystal of zinc sulphate is thrown into a supersaturated solution of the ferrous salt, but, on the other hand, if a crystal of copper sulphate be employed, asymmetric crystals having the composition $FeSO_4+5H_2O$ are obtained (Lecoq de Boisbaudran). These last are also deposited when a solution of ferrous sulphate containing free sulphuric acid is allowed to evaporate in a vacuum. Crystals of green vitriol first separate, and then the penta-hydrated salt, whilst at last

crystals of a tetra-hydrate, $FeSO_4+4H_2O$, are deposited, and these are isomorphous with the corresponding manganese sulphate. When ferrous sulphate is heated in a vacuum to 140°, it yields a white powder of the monohydrate $FeSO_4+H_2O$, and this, when gently heated in absence of air, yields the anhydrous salt $FeSO_4$. The monohydrate is, moreover, precipitated by the addition of strong sulphuric acid to a saturated solution of the salt.[1] When the heptahydrate is melted in its water of crystallisation and allowed to cool, the anhydrous salt is deposited. Hydrates with $2H_2O$ and $3H_2O$ have also been described. When the heptahydrate is exposed to the air, it gradually loses water and becomes converted into basic ferric sulphate.

Ferrous sulphate is insoluble in concentrated sulphuric acid and absolute alcohol, whilst it dissolves slightly in dilute alcohol. Hence sulphuric acid and alcohol precipitate the solution of the sulphate, the precipitate containing varying quantities of water of crystallisation according to the quantity of the precipitant and the concentration of the solution. A solution of ferrous sulphate, like the chloride, absorbs nitric oxide. The dark brown saturated solution, which probably contains the compound $FeSO_4.NO$, gives off the gas in a vacuum as well as when heated; in the latter case small quantities of nitrogen monoxide and ferric sulphate are formed. When the brown solution is mixed with strong sulphuric acid, care being taken to keep the mixture cool, it becomes of a purple-red colour; and upon this reaction the well-known test for nitric acid and the nitrates depends, as well as the method of detecting the presence of nitrous fumes in sulphuric acid.

Green vitriol is largely used in the arts and manufactures for the preparation of iron-mordants, inks, Prussian blue, &c.

Ferrous sulphate in common with the sulphates of the metals of the magnesium group, and the sulphates of copper and manganese, forms, with the sulphates of the alkali-metals, well crystallising double-salts, of which the following is the most important:—

Ferrous Ammonium Sulphate, $FeSO_4+(NH_4)_2SO_4+6H_2O$, is obtained when the calculated quantities of ammonium sulphate and green vitriol are dissolved in the minimum quantity of hot water, and the filtered solution allowed to crystallise or precipitated with alcohol. It forms clear, hard, bluish-green monosym-

[1] Etard, *Compt. Rend.* 1878, **87**, 502; Scott, *Journ. Chem. Soc.* 1897, **1**, 564.

metric crystals, which have a specific gravity of 1·813. One hundred parts of water dissolve (Tobler):—

At	0°	20°	30°	60°	75°
$FeSO_4+(NH_4)_2SO_4$.	12·2	21·6	28·1	44·6	56·7

This salt is a very stable one, and does not readily undergo alteration in the air, being much less easily oxidised than green vitriol itself. Hence it is largely used instead of the latter salt for the purposes of volumetric analysis.

Ferrous Disulphate, FeS_2O_7, separates out as a white powder when a concentrated solution of iron sulphate is mixed with several times its volume of concentrated sulphuric acid. It forms microscopic prisms, and is decomposed by water into sulphuric acid and green vitriol.[1]

560 *Ferric Sulphate*, $Fe_2(SO_4)_3$, is obtained by the action of nitric acid on a hot solution of green vitriol, to which the requisite quantity of sulphuric acid has been added:

$$6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+2NO+4H_2O.$$

The yellowish brown solution gives a syrupy liquid when concentrated, from which colourless crystals are deposited on standing. When these are heated, or when sulphuric acid is added to the concentrated solution, the anhydrous salt is formed as a white powder, whilst by the action of green vitriol on boiling sulphuric acid the same salt is deposited in small crystalline scales or rhombic prisms:

$$2FeSO_4+2H_2SO_4=Fe_2(SO_4)_3+SO_2+2H_2O.$$

The anhydrous salt dissolves slowly in water and it is decomposed on heating into ferric oxide and sulphur trioxide. When a dilute solution of ferric sulphate is boiled or incompletely precipitated with alkalis, or when a solution of green vitriol is allowed to oxidise in the air, various basic ferric sulphates are formed. An iron mordant obtained by oxidising green vitriol with nitric acid deposits on standing large transparent crystals, which are probably monosymmetric, having the composition $FeSO_4(OH)+7H_2O$; these are decomposed by water with formation of the insoluble salt $Fe_2SO_4(OH)_4+5H_2O$.[2] Various other basic ferric sulphates occur as minerals, being formed by the oxidation of the sulphides of iron. Amongst these may be mentioned vitriol ochre, $FeSO_4(OH)_4+2Fe(OH)_3+H_2O$. This

[1] Bolas, *Journ. Chem. Soc.* 1874, 212. [2] *Ber.* 1875, **8**, 77.

frequently occurs in long brown, green, or ochreous yellow stalactites; whilst copiapite, $Fe_2(SO_4)_3+Fe_2(SO_4)_2(OH)_2+10H_2O$, occurs in sulphur yellow tables or crystalline scales, and fibroferrite, $2Fe_2(SO_4)_2(OH)_2+Fe_2SO_4(OH)_4+24H_2O$, forms a pale-yellow or nearly white pearly or silky mass.

Ferroso-ferric Sulphates.—The two sulphates of iron form various double salts, of which some are found in the mineral kingdom. Amongst these is roemerite, $Fe_3(SO_4)_4+12H_2O$, forming yellow monosymmetric crystals, occurring at the Rammelsberg mine, near Goslar, together with another similar mineral termed voltaite, in which a part of the iron is replaced by isomorphous metals.

Ferric Potassium Sulphate or *Iron Alum*, $Fe_2(SO_4)_3+K_2SO_4+24H_2O$, is obtained when the proper quantity of potassium sulphate is added to a solution of ferric sulphate and the concentrated solution allowed to stand for some days about 0°. The salt forms bright violet octohedra, and dissolves in about five parts of cold water. If caustic potash be added to the solution and the dark liquid allowed to evaporate, transparent yellowish-brown hexagonal crystals separate out which have the composition $5K_2SO_4+2Fe_2(SO_4)_2(OH)_2+16H_2O$, and possess the peculiar optical properties of tourmaline. This salt easily decomposes into iron-alum and an insoluble basic ferric salt.

Several salts with ammonium sulphate have also been described.[1]

Iron and the Elements of the Nitrogen Group.

561 *Iron Nitride*, Fe_2N. Bertholet noticed that when ammonia is passed over ignited iron wire it is converted into its elements and the iron becomes brittle. This depends upon the fact that at a low temperature iron nitride is formed, and this is decomposed again at a higher point. In order to prepare the nitride, ferrous or ferric chloride is heated to a temperature below redness in a current of dry ammonia. A silver-white brittle mass is thus obtained having a specific gravity of 5·0, and this when brought in the state of powder into a gas-flame ignites with emmission of bright sparks. When heated in hydrogen pure iron is left. Iron nitride has a specific gravity of 6·03, and is so soft that it may be cut with a knife;[2] it is

[1] Lachaud and Lepierre, *Compt. Rend.* 1892, **114**, 915.

[2] Stahlschmidt, *Pogg. Ann.* 1865, **125**, 37.

magnetic and oxidises very easily in the air, dissolving in nitric acid with evolution of nitric oxide, and also in dilute hydrochloric acid with formation of hydrogen, ferrous chloride, and ammonium chloride. Aqueous vapour converts it at a red-heat into black magnetic oxide.

Another iron nitride, having the composition Fe_5N_2, occurs as a lustrous metallic deposit on the lavas of Etna. It may be artificially prepared by heating the lava in a current of hydrochloric acid and then leading ammonia over the strongly heated mass. It is likewise formed, although with greater difficulty, when the lava is ignited in a current of sal-ammoniac vapour.[1] It is also obtained as a feebly magnetic grey powder when reduced iron is heated in ammonia.[2]

Ferrous Nitrate, $Fe(NO_3)_2+6H_2O$, is best obtained by the decomposition of green vitriol with barium nitrate, the filtrate being evaporated in a vacuum over sulphuric acid. It is very soluble in water and very unstable, easily passing into ferric nitrate. When iron is dissolved in cold dilute nitric acid, the following reaction takes place (Berzelius):

$$8Fe+20HNO_3=8Fe(NO_3)_2+2NH_4NO_3+6H_2O,$$

but the reaction varies greatly with the concentration of the acid and the temperature.[3]

Ferric Nitrate, $Fe(NO_3)_3$, is formed by dissolving iron in nitric acid. The brown concentrated solution deposits, on addition of nitric acid, according to the quantity of the same or the concentration of the solution, colourless cubes of $Fe(NO_3)_3+6H_2O$, or colourless monosymmetric crystals containing 9 molecules of water. These are very deliquescent, and dissolve in water forming a brown liquid, which becomes colourless when concentrated nitric acid is added to it. Ferric nitrate is used as a mordant in dyeing and calico-printing.

Several soluble and several insoluble basic ferric nitrates are known.

Iron-nitroso-sulphides.—These compounds, discovered by Roussin, are obtained when the nitrites and sulphides of the alkali metals act upon iron salts, in the same way as the nitroprussides are formed by the action of the nitrites and cyanides on iron compounds. The constitution of these compounds has

[1] Silvestri, *Pogg. Ann.* 1876, **157**, 165.
[2] Fowler, *Chem. News*, 1894, **68**, 152.
[3] Montemartini, *Journ. Chem. Soc.* 1892, ii. 1278.

not been satisfactorily ascertained, although they have been analysed by several chemists.[1] They appear, however, to be the salts of two complex acids, iron heptanitrososulphydric acid, $Fe_4(NO)_7S_3H$, and iron tetranitrososulphydric acid, $Fe_2(NO)_4S_2H_2$. The substance formerly described as iron nitrosothiocarbonate appears to be identical with the sodium salt of the heptanitroso-acid.

Potassium Iron Heptanitrososulphide, $K[Fe_4(NO)_7S_3]+H_2O$, is obtained by adding a solution of ferrous sulphate to a solution of sodium nitrite and potassium sulphide. It forms dark, monosymmetric crystals with a diamond lustre, and is only sparingly soluble in water. Dilute sulphuric acid precipitates from its solution the free iron heptanitrososulphydric acid as an amorphous brown mass. When the potassium salt is heated with concentrated sulphuric acid, it yields nitric oxide, nitrogen, sulphuretted hydrogen, sulphur, ferric sulphate, ammonium sulphide, and potassium sulphate.

Potassium Iron Tetranitrososulphide, $K_2[Fe_2(NO)_4S_2]+4H_2O$, is obtained by the action of caustic potash on the foregoing salt. It forms dark red crystals, and is insoluble in water. It decomposes violently when heated, forming ammonium sulphate, potassium sulphate, and other products. The free acid decomposes slowly in the cold into sulphuretted hydrogen, nitrogen, nitrous oxide, and the heptanitroso-acid.

562 *Phosphides of Iron.*—In the year 1780, J. C. F. Meyer, whilst examining the cause of the cold-shortness of iron, came to the conclusion that this was produced by the presence of a peculiar metal to which he gave the name *hydrosiderum*. The subject was investigated shortly afterwards by Bergman, who found that when the residue obtained by dissolving cold-short iron in sulphuric acid, is fused before the blowpipe with reducing agents a metallic bead is obtained which he also believed to be a peculiar metal to which he gave the name of *siderum*. In 1784, Meyer repeated his experiments and came to the conclusion that the substance thus obtained was a compound of iron and phosphoric acid, and it was afterwards ascertained that the body got by reduction on charcoal is a phosphide of iron.

This compound, which has the composition Fe_2P, is obtained

[1] Roussin, *Compt. Rend.* 1858, **46**, 224; Proczinsky, *Annalen*, 1863, **125**, 302; Rosenberg, *Ber.* 1870, **3**, 312; Pavel, *Ber.* 1882, **15**, 2600; Marie and Marquis, *Compt. Rend.* 1896, **122**, 137.

by fusing a ferrous or ferric phosphate together with lamp-black, under a layer of chloride of sodium. It is a porous, metallic, non-magnetic powder, which when heated in the air is converted into a basic phosphate, $2Fe_2O_3,P_2O_5$. When iron pyrites or iron powder is ignited in a stream of phosphuretted hydrogen a grey non-magnetic powder, having the composition Fe_3P_4, is obtained, whilst the compound FeP is prepared as a dark-grey powder when the monosulphide is ignited in the same gas, or when iron is heated in phosphorus vapour. These various phosphides of iron do not undergo alteration in the air. They dissolve in hot hydrochloric acid with formation of hydrogen phosphide and phosphoric acid, and they can be fused in all proportions with iron.[1] Several other compounds which have been described are mixtures of phosphide with metallic iron.

Ferrous Phosphate, $Fe_3(PO_4)_2+8H_2O$, occurs as the mineral vivianite, crystallising in monosymmetric prisms. In its pure state it is colourless, but it generally possesses a green or blue tint, owing to partial oxidation. It is also found as an earthy mass termed blue iron-earth, sometimes dispersed through clay, and together with bog-iron ore, and in the cavities in fossil bones. When a solution of green vitriol is precipitated with sodium phosphate, a white precipitate is obtained, which, however, soon becomes blue or green on exposure to air. If the liquid and the precipitate be allowed to stand together for a week at a temperature of from 60° to 80° the compound is converted into small crystals which become coloured blue on exposure to the air (Debray). The precipitated phosphate is used in medicine.

When iron is dissolved in a solution of phosphoric acid, colourless needles, having the composition $Fe(H_2PO_4)_2+2H_2O$, are deposited after some time, and these rapidly alter on exposure to air.[2]

Ferric Phosphates.—The normal orthophosphate, $FePO_4+2H_2O$, is obtained as a yellowish white precipitate by adding ordinary sodium phosphate to normal ferric chloride. It is soluble in dilute mineral acids, but not in cold acetic acid, and is slowly decomposed by water. When ferric hydroxide is dissolved in ortho-phosphoric acid and the solution rapidly evaporated, the diacid salt, $Fe(H_2PO_4)_3$, is obtained as a pink crystalline powder, which decomposes in moist air and deposits

[1] Freese, *Pogg. Ann.* 1867, **132**, 225.
[2] Erlenmeyer, *Annalen*, 1878, **194**, 182.

crystals of the monacid salt, $2FeH_3(PO_4)_2+5H_2O$ (Erlenmeyer). Ferric metaphosphate, $Fe(PO_3)_3$, is deposited in pink plates when ferric hydroxide is digested with glacial phosphoric acid at 100°[1]

Basic iron phosphates occur in nature, and frequently form a constituent of limonite. It also occurs as dufrenite, $Fe_2(OH)_3PO_4$, which is found sometimes in rhombic crystals, but more generally in needles or as a radiated fibrous mass. Vivianite is often oxidised and is converted into beraunite, $Fe(PO_4)+2Fe_2PO_4(OH)_3+4H_2O$, occurring in small foliated aggregates having a hyacinth-red colour.

563 *Arsenides of Iron.*—When metallic iron is ignited with an excess of arsenic in the absence of air, a white and very brittle mass of FeAs is obtained. Lölingite or $FeAs_2$ occurs as a mineral crystallised in silver-white rhombic prisms. Mispickel or arsenical pyrites Fe_2AsS_2 is a more common mineral; it crystallises in short rhombic prisms of a silver-white colour. A portion of the iron is frequently replaced by cobalt, and this mineral serves as the chief source of the arsenical compounds.

Ferric Arsenite.—The basic salt, $Fe_4O_5(OH)_5As=4Fe_2O_3+As_2O_3+5H_2O$, is a voluminous brown precipitate closely resembling ferric hydroxide in appearance. It is obtained by adding an aqueous solution of arsenious oxide, or an arsenite, to ferric acetate. This compound is also formed when a solution of arsenious oxide is shaken with freshly precipitated ferric hydroxide, and for this reason this latter compound is used as an antidote in case of arsenical poisoning. (See vol. i., 627).

Ferric Arsenates.—The normal arsenate occurs as scorodite $Fe(AsO_4)+2H_2O$, in brown rhombic vitreous crystals. Basic arsenates are also found in the mineral kingdom; amongst these we have iron-sinter or pharmacosiderite, $3FeAsO_4+Fe(OH)_3+6H_2O$, which occurs crystallised in the regular system in green or brownish-green adamantine crystals. The acid arsenate, $2Fe_2(HAsO_4)_3+9H_2O$, is a white precipitate obtained by adding hydrogen disodium arsenate to a solution of ferric chloride. It is easily soluble in hydrochloric acid, and separates on evaporation as a white powder.

[1] Hautefeuille and Margotte, *Compt. Rend.* 1888, **106**, 138. See also Johnson, *Ber.* 1889, **22**, 976.

Iron and Boron.

564 *Iron Boride*, FeB, is formed when the vapour of boron chloride is passed over iron at a dull red heat, or when soft iron is heated with boron in the electric furnace. It is thus obtained as an amorphous powder or in yellowish grey crystals of specific gravity 7·15. It oxidises slowly in moist air and dissolves in concentrated acids.[1] When grey cast iron is heated with boron, the latter replaces the carbon to a considerable extent.[2]

Iron and Carbon.

565 *Iron Carbide*, Fe_3C, exists in white cast iron and steel, and can be extracted from the latter of these by the action of dilute acids.[3] This is best carried out by placing the steel in dilute hydrochloric acid and connecting it with the carbon of a Bunsen's cell, the cathode being a platinum plate. It has also been prepared by heating iron in a carbon crucible in the electric furnace and suddenly cooling the metal. When the cooled mass is treated with dilute acids, the carbide is left undissolved (Moissan). The crystals of the carbide can be distinctly recognised under the microscope in polished sections of steel.

It forms either a greyish powder or hard bright silvery plates, and dissolves in more concentrated acid, hydrogen being evolved mixed with hydrocarbons of the general formulæ C_nH_{2n} and C_nH_{2n+2}.[4] Fuming nitric acid has no action on it. It seems probable that a subcarbide of iron, $Fe_{24}C$, also exists in hardened steel, which is more readily decomposed by acids than the normal carbide (Arnold).

Ferrous Carbonate, $FeCO_3$, occurs naturally as spathic iron-ore, which, however, contains larger or smaller quantities of the carbonates of calcium, manganese, and magnesium. The mineral is obtained artificially in microscopic rhombohedra by precipitating a solution of green vitriol with sodium bicarbonate and heating the mixture for twelve to thirty-six hours at a tem-

[1] Moissan, *Compt. Rend.* 1895, **120**, 173.

[2] Moissan, *Compt. Rend.* 1894, **119**, 1172.

[3] Abel and During, *Proc. Inst. Mech. Eng.* 1885, 30; Arnold and Read, *Journ. Chem. Soc.* 1894, **1**, 788.

[4] Mylius, Foerster and Schoene, *Ber.* 1896, **29**, 2991; Campbell, *Amer. Chem. Journ.* 1896, **18**, 536.

perature of 150° (Sénarmont). When a cold solution of pure ferrous sulphate is precipitated with sodium carbonate, a flocculent white precipitate is thrown down which rapidly becomes of a dirty green colour from absorption of oxygen from the air and evolution of carbon dioxide, at last being wholly converted into ferric hydroxide. If the precipitate be washed in total absence of air, it may be obtained pure and colourless. Usually, however, it takes the form of a greyish powder, which is soon oxidised on exposure to the air. If the moist precipitate be mixed with sugar it does not undergo such rapid change.

Ferrous bicarbonate exists in many mineral waters, and is formed in solution by the action of carbonic acid on ferrous carbonate. When such a solution is exposed to the air, carbonic acid gas is evolved and ferric hydroxide deposited.

Ferric Carbonate is not known in the dry state, since the precipitate produced by the addition of a soluble carbonate to a ferric salt rapidly loses carbonic acid.

Iron Pentacarbonyl, $Fe(CO)_5$, is formed in small amount when iron, obtained by the reduction of ferrous oxalate, is allowed to stand in contact with carbonic oxide, and then heated at 120°.[1] It is a viscous liquid which boils at 102·8° (at 749 mm.), solidifies below −21° to a mass of yellowish needles, and has a specific gravity of 1·4664 at 18°. When its vapour is heated at 180° it decomposes into carbonic oxide and metallic iron, which is deposited as a mirror on the walls of the containing vessel. It dissolves in alcohol and ether, and is slowly decomposed on exposure to the air, ferric hydroxide being deposited. It is unattacked by dilute acids, but is converted by chlorine, bromine and nitric acid into the corresponding ferric salts. When exposed to the light, carbonic oxide is evolved and golden yellow tablets deposited, which consist of *diferroheptacarbonyl*, $Fe_2(CO)_7$, and cannot be volatilised without decomposition.

Iron carbonyl is also frequently found in water-gas[2] and coal-gas which has been compressed in iron cylinders. Such gas deposits ferric oxide when it is burned.

[1] Mond and Quincke, *Journ. Chem. Soc.* 1891, i. 604; Mond and Langer, *Journ. Chem. Soc.* 1891, i. 1090.

[2] Roscoe and Scudder, *Proc. Chem. Soc.* 1891, 126.

Iron and Cyanogen.

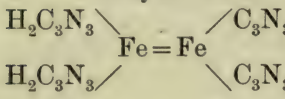
566 Our knowledge of the peculiar compounds of iron and cyanogen commences with the discovery of Prussian blue, which, as has been stated (vol. i., p. 747), was made early in the 18th century by a colour-maker named Diesbach. In 1752 Macquer observed that when this colour is boiled with caustic potash oxide of iron remains, whilst a peculiar salt enters into solution which was named phlogisticated alkali or yellow prussiate of potash. This body was shown to contain iron and prussic acid by Berthollet in 1787. Proust, in 1806, next found that iron remains in combination with prussic acid when the alkali in the yellow prussiate is replaced by other bases; and Ittner in 1809 considered that the compounds of ferric oxide and other bases with prussic acid are double salts. In opposition to this view R. Porret[1] in 1814–15 published a series of experiments founded on a suggestion of Berthollet's, from which he drew the conclusions that the so-called double prussiates containing iron are simple salts of a compound acid containing ferrous oxide and prussic acid, to which he gave the name of *ferruretted chyazic acid*, a name derived from the fact that it is a compound of carbon, hydrogen, and azote or nitrogen. Gay-Lussac's classical investigation of prussic acid followed immediately on Porret's memoir. In this he proved that the acid is a hydrogen compound of the radical cyanogen. Berzelius then showed that all the salts of iron and prussic acid may be considered to be double cyanides, and that (according to our present nomenclature) the prussiate of potash is a cyanide of iron and potassium, $Fe(CN)_2 + 4KCN$. Three years later Gmelin[2] obtained a new compound by acting upon this salt with chlorine, which from its red colour was termed red prussiate of potash. This may be regarded as the ferric double salt, $Fe(CN)_3 + 3KCN$. Gmelin likewise proved that the potassium in the salt may be replaced by hydrogen, thus giving rise to ferricyanic acid. In the following year Gay-Lussac pointed out that the yellow prussiate may be supposed to contain a compound radical consisting of iron and cyanogen, to which he gave the name *cyanoferre*. Liebig extended this explanation to the other cyanogen compounds containing iron, and considered the above salts as compounds of two isomeric

[1] *Phil. Trans.* 1814, 527; *Ann. Phil.* **12**, 214, and **14**, 295.
[2] *Schweigg. Journ.* **34**, 325.

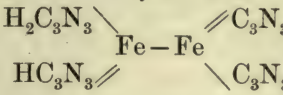
radicals, C_6N_6Fe, to which he gave the names of *ferrocyanogen* and *ferridcyanogen*, indicating their composition by the symbols Cfy and Cfdy.[1]

Graham[2] assumed that these compounds contained the radical of cyanuric acid, tricyanogen, C_3N_3, to which he gave the name of *prussine*. If we suppose that each valency of the tetrad group $=Fe-Fe=$ is combined with the triad group tricyanogen, the octad radical ferrocyanogen is produced; and in a similar way, the hexad ferricyanogen is formed by the combination of the six valencies of the hexad group $\equiv Fe-Fe\equiv$, with four tricyanogen groups. The acids which are thus formed have then the following constitutions (Erlenmeyer).[3]

Ferrocyanic Acid.



Ferricyanic Acid.



On the more modern supposition that iron in the ferrous salts is a dyad and in the ferric salts a triad, similar formulæ, but representing only half the molecular weight of the above, are obtained.

Ferrocyanic Acid. $(H_2C_3N_3)_2Fe$

Ferricyanic Acid. $H_2C_3N_3{\cdot}Fe=C_3N_3H.$

Various other suppositions have been made with regard to the constitution of these compounds, especially respecting the mode of association of the cyanogen groups with the iron, but little experimental evidence can be adduced in favour of these views. Ferrocyanic acid itself behaves as a moderately strong tetrabasic acid,[4] and therefore yields the ions $4\overset{+}{H}$ and $[\overset{--}{Fe(CN)_6}]$.

The ferrocyanogen compounds, therefore, may be represented as having the general formula $\overset{\text{I}}{R}_4[\overset{\text{IV}}{Fe}(CN)_6]$, whilst the ferricyanogen compounds probably correspond to the analogous formula $\overset{\text{I}}{R}_3[\overset{\text{III}}{Fe}(CN)_6]$, the exact constitution of the acid radicals $[\overset{\text{IV}}{Fe}(CN)_6]$ and $[\overset{\text{III}}{Fe}(CN)_6]$ being at present unknown.

[1] *Handworterbuch*, **3**, 66.
[2] *Elements of Chemistry*, **1**, 200.
[3] *Lehrbuch Org. Chem.* 1867, 148.
[4] Ostwald, *Lehrbuch* **2**, 851.

Ferrocyanogen Compounds.

567 Until recent years the ferrocyanides served as the point of departure for the preparation of almost all the other cyanogen compounds, and they are still manufactured on the large scale, although the cyanides specially required for the extraction of gold are at present largely obtained in other ways. Formerly, the only ferrocyanides obtained on the large scale were those of potassium and iron, but at present the sodium salt is also prepared in quantity.

The method adopted for the manufacture of the potassium salt, frequently known as yellow prussiate of potash, was as follows:—Crude potashes were heated in hemispherical iron pots closed by an iron lid, having an aperture through which a mixture of iron filings and animal matter, such as horns, feathers, dried blood and leather clippings, was added from time to time. The reaction is very complex, and has not received a complete explanation; it appears, however, that part of the nitrogen of the organic matter is evolved as ammonia, whilst another portion combines with potassium and carbon, forming potassium cyanide; simultaneously the sulphur of the organic matter, as well as that in the potassium sulphate, always present in crude potashes, gives rise to potassium iron sulphide, $K_2S + Fe_2S_3$. When the resulting fused mass or "metal" is lixiviated, the cyanide and sulphide interact as follows:—

$$13KCN + Fe_2S_3 = 2K_4Fe(CN)_6 + 2K_2S + KCNS.$$

The solution is evaporated to a specific gravity of 1·27, and run into crystallising vessels, where the crude salt is deposited and this is purified by recrystallisation, the mother liquors being employed to dissolve fresh quantities of the crude salt.

In this process part of the nitrogen is lost as ammonia, and a further loss occurs owing to the formation of cyanate and thiocyanate, and many attempts have been made to improve the process and obviate these sources of loss, but without much success. At the present time the manufacture of ferrocyanides by this method is gradually dying out, as these are now obtained as bye products in the coal-gas manufacture, and other industries in which coal is subjected to destructive distillation. The unpurified gas usually contains a small quantity of cyanogen compounds, chiefly if not entirely as hydrocyanic acid. When

the gas is purified by means of ferric oxide (vol. i, p. 777) this is absorbed, together with the sulphuretted hydrogen, and when the absorbing oxide is completely spent it is frequently found to contain sufficient Prussian blue to repay the cost of extraction. A number of proposals for this purpose have been patented, which all depend on the fact that Prussian blue is converted by the action of alkalis into the ferrocyanide of the alkali employed, which is then purified in the usual manner. In recent years the hydrocyanic acid has been extracted at a number of gas works, by passing the gas, previous to the dry purification (vol. i, p. 776), through a suitable apparatus in which it is brought into intimate contact with an alkaline liquid, containing an iron salt in suspension. The iron salt is converted into ferrous sulphide by the action of the sulphuretted hydrogen in the crude gas, and this is acted on by the hydrocyanic acid in presence of alkali (*e.g.* potash) as follows:

$$FeS + 6HCN + 2K_2CO_3 = K_4Fe(CN)_6 + H_2S + 2CO_2 + 2H_2O.$$

The potash may be replaced by sodium carbonate or lime, in which case sodium or calcium ferrocyanide is obtained, and if the gas be treated before the removal of ammonia, the latter supplies the necessary alkali, a solution of ammonium ferrocyanide being formed. The liquid after separation of insoluble matter, may be evaporated to a cake or to the point of crystallisation, or it may be precipitated as Prussian blue by the addition of a ferric salt.

Hydrogen Ferrocyanide or Ferrocyanic Acid, $H_4[Fe(CN)_6]$ This is best obtained when pure hydrochloric acid is added to an equal volume of a cold saturated solution of potassium ferrocyanide. The precipitate which forms is dried on a porous plate in absence of air, then dissolved in alcohol, and precipitated by ether.[1] It is a white powder crystallising in small needles. Larger crystals may be obtained by pouring a layer of ether on to the alcoholic solution. Ferrocyanic acid is easily soluble in water and alcohol. It possesses a strongly acid taste and reaction, and is so powerful an acid that it liberates not only acetic, but even oxalic acid from its salts. It oxidises quickly on exposure to air, especially when warmed with formation of hydrocyanic acid and ferric ferrocyanide:

$$7H_4Fe(CN)_6 + O_2 = 24HCN + Fe_7(CN)_{18} + 2H_2O.$$

[1] Liebig, *Annalen*, 1853, **87**, 127.

This reaction is employed in calico-printing, the cloth being printed with a mixture of tartaric acid and yellow prussiate, and then steamed.

When the solution of the acid is boiled, hydrocyanic acid is evolved and a white precipitate of acid ferrous ferrocyanide remains behind :[1]

$$2H_4[\overset{iv}{Fe}(CN)_6] = 6HCN + H_2\overset{ii}{Fe}[\overset{iv}{Fe}(CN)_6]$$

This decomposition explains the preparation of prussic acid by the action of dilute sulphuric acid on the ferrocyanide.

Potassium Ferrocyanide, or *Yellow Prussiate of Potash,* $K_4Fe(CN)_6 + 3H_2O$. The methods of manufacture of this salt have already been described.

It is also formed when a ferrous salt is mixed with an excess of potassium cyanide. In this case a brown precipitate is first formed, which was supposed to be ferrous cyanide, but is now known to contain potassium cyanide, and probably has the formula $Fe_2(CN)_5K$. This readily dissolves in potassium cyanide :

$$Fe_2(CN)_5K + 7KCN = 2K_4Fe(CN)_6.$$

A solution of potassium cyanide in absence of air dissolves metallic iron with evolution of hydrogen slowly in the cold and more quickly when heated :

$$6KCN + Fe + 2H_2O = K_4FeCy_4 + 2KOH + H_2.$$

Potassium ferrocyanide forms quadratic pyramids in which the basal faces are usually dominant, Fig. 180. They are of a lemon yellow colour, and generally opaque. Small crystals, on the other hand, are amber-coloured and transparent. The specific gravity is 1·83. It does not undergo alteration in pure air at the ordinary temperature, but what heated to 60° it begins to lose its water of crystallisation, which is completely given off at 100°, the anhydrous salt remaining as a white powder. It has a sweetish saline and somewhat bitter taste, and is not poisonous, acting in large doses as an aperient. Four parts of cold, and two parts of boiling water dissolve the salt, which is insoluble in alcohol, and is precipitated from aqueous solution by this liquid in yellowish-white pearly scales.

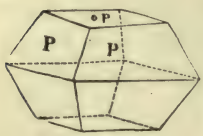


Fig. 180.

[1] Reimann and Carius, *Annalen,* 1860, **113**, 39.

When its solution is exposed to light for some time Prussian blue separates out, and on long-continued boiling of the solution in the air ammonia is given off and the liquid becomes alkaline. The commercial salt frequently contains considerable quantities of potassium sulphate which can be removed by recrystallisation only with difficulty.

Potassium ferrocyanide in addition to its use in the preparation of Prussian blue, and other cyanogen compounds, is employed in calico-printing, and also for the case hardening of iron.

Sodium Ferrocyanide, $Na_4Fe(CN)_6$, is manufactured in the manner described above, and may also be obtained by boiling Prussian blue with caustic soda or sodium carbonate. It crystallises readily in yellow monosymmetric prisms, which were stated by Bunsen to contain 12 molecules of water; Pebal[1] has, however, shown that the true formula is $Na_4Fe(CN)_6+10H_2O$. It is commercially known as yellow prussiate of soda.

Ammonium Ferrocyanide, $(NH_4)_4Fe(CN)_6+3H_2O$, is obtained by the action of ammonia on ferrocyanic acid or on Prussian blue, and crystallises in yellow prisms isomorphous with the potassium salt. Its solution readily decomposes on heating with evolution of ammonium cyanide.

Ammonium Potassium Ferrocyanide, $(NH_4)K_3Fe(CN)_6$, is formed when an ammoniacal solution of potassium ferricyanide is treating with reducing agents such as grape sugar. It forms quadratic prisms which readily dissolve in water.

Calcium Ferrocyanide, $Ca_2Fe(CN)_6+12H_2O$, is formed when Prussian blue is boiled with the requisite quantity of milk of lime, or by passing hydrocyanic acid into a mixture of slaked lime and ferrous hydroxide suspended in water. It forms yellow asymmetric prisms, one part of which dissolves in 0·66 parts of water at 90°, and which are even more soluble in cold water.

Potassium Calcium Ferrocyanide, $K_2CaFe(CN)_6+3H_2O$, and *Ammonium Calcium Ferrocyanide*, $(NH_4)_2CaFe(CN)_6+3H_2O$, are obtained as white crystalline precipitates, which are very sparingly soluble in water, when calcium chloride is added to a moderately concentrated solution of potassium or ammonium ferrocyanide, or by the addition of potassium or ammonium chlorides to a solution of calcium ferrocyanide.

Strontium Ferrocyanide, $Sr_4Fe(CN)_6+15H_2O$, is prepared in a similar way to the calcium salt, and forms fine monosymmetric readily soluble crystals.

[1] *Annalen*, 1886, **233**, 160.

Barium Ferrocyanide, $Ba_2Fe(CN)_6+3H_2O$, is obtained by boiling Prussian blue with baryta water, or by the action of ferrous sulphate on barium cyanide. It forms flat monosymmetric prisms which dissolve in 580 parts of cold, and 116 parts of boiling water.

Barium Potassium Ferrocyanide, $K_2BaFe(CN)_6+3H_2O$. This salt is deposited in small yellow rhombohedra when boiling saturated solutions of 2 parts of ferrocyanide of potassium and 1 part of barium chloride are mixed, and the mixture allowed to cool. It dissolves in 38 parts of cold, and 9·5 parts of boiling water. This salt is employed for the preparation of the other double ferrocyanides of potassium, which may all be obtained by the action of the corresponding sulphates upon the salt. When a hot solution of ferrocyanide of potassium is treated with an excess of barium chloride, a mixture of the double salt with barium ferrocyanide is obtained, and the whole is converted into the latter salt when the precipitate is boiled with a solution of barium chloride.

Zinc Ferrocyanide, $Zn_2Fe(CN)_6$, is a white precipitate used in medicine.

Copper Ferrocyanide, $Cu_2Fe(CN)_6+10H_2O$, is a fine brown precipitate known as Hatchett's brown.

A large number of other ferrocyanides and double ferrocyanides have been prepared, many of which crystallise well.[1] Those of the heavy metals are mostly sparingly soluble or insoluble precipitates, some of which possess characteristic colours, as in the case of copper and uranium, and potassium ferrocyanide is therefore used as a reagent for these metals. The ferrocyanides of iron are described below.

Ferricyanogen Compounds.

568 *Ferricyanic Acid*, $H_3[Fe(CN)_6]^{iii}$ or H_3Cfdy. This is obtained by decomposing the lead salt with dilute sulphuric acid, and evaporating the solution at a moderate temperature. The acid crystallises in brown needles and has an astringent acid taste.

Potassium Ferricyanide, $K_3[Fe(CN)_6]^{iii}$, is frequently known under the name of *red prussiate of potash*, and is formed when

[1] Wyruboff, *Ann. Chim. Phys.* 1869 (4), **16**, 280; 1870 (4), **21**, 270; 1876 (5), **8**, 445.

potassium ferrocyanide is treated with oxidising agents. It is obtained on the large scale by passing chlorine into a solution of the yellow prussiate:

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl.$$

It may be readily separated from the potassium chloride formed at the same time by repeated crystallisation. It forms large dark red monosymmetric prisms (Figs. 181 and 182), which have a specific gravity of 1·8, and frequently occurs in the twin forms exhibited by Fig. 182. It possesses a faintly astringent and saline taste, and yields a dark yellow powder. It dissolves in water giving a yellowish-brown solution, which on dilution

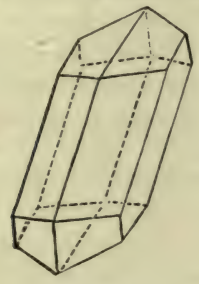


FIG. 181.

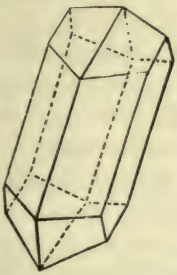


FIG. 182.

assumes a lemon-yellow colour. One hundred parts of water dissolve:[1]

At	4°·4	10°	15°·6	37°·8	100°
$K_3Fe(CN)_6$	33·0	36·6	39·7	58·8	77·6

and 82 parts at 104°, the boiling-point of the saturated solution. It is only slightly soluble in alcohol. When exposed to light the solution becomes darker, and a blue precipitate is formed, ferrocyanide remaining in solution. When the salt is heated in a flame it burns, and when mixed with ammonium nitrate and heated, the mixture detonates. It is a powerful oxidising agent, especially in alkaline solution, converting the monoxides of lead and manganese into dioxides, and forming potassium chromate and ferrocyanide of potassium when boiled with solution of chromium sesquioxide in potash:

$$6K_3Fe(CN)_6 + Cr_2O_3 + 10KOH = 6K_4Fe(CN)_6 + 2K_2CrO_4 + 5H_2O.$$

[1] Wallace, *Journ. Chem. Soc.* 1855, 80.

When its solution is acted upon by sodium amalgam, sodium potassium ferrocyanide is formed. Hydrogen dioxide converts potassium ferricyanide into ferrocyanide:

$$4K_3Fe(CN)_6 + 2H_2O_2 = 3K_4Fe(CN)_6 + H_4Fe(CN)_6 + 2O_2,$$

whilst on the other hand hydrogen dioxide oxidises a neutral solution of the yellow salt to ferricyanide (Weltzien):

$$2K_4Fe(CN)_6 + H_2O_2 = 2K_3Fe(CN)_6 + 2KOH.$$

Sodium Ferricyanide, $2Na_3[Fe^{III}(CN)_6] + H_2O$, is obtained by the action of chlorine upon sodium ferrocyanide. It dissolves in 1·25 parts of boiling, and 5·3 parts of cold water, and crystallises in ruby-red four-sided prisms which deliquesce on exposure to air.

Potassium Sodium Ferricyanide, $Na_3Fe(CN)_6 + K_3Fe(CN)_6$ crystallises in fine red cubes which are formed when the sodium and potassium salts are allowed to crystallise together.

Ammonium Ferricyanide, $2(NH_4)_3Fe(CN)_6 + H_2O$, is obtained in a similar way to the other ferricyanides. It forms fine red monosymmetric prisms, easily soluble in water and permanent in the air.

Lead Ferricyanide, $Pb_3[Fe(CN)_6]_2 + 16H_2O$, is formed by mixing hot solutions of the potassium salt and lead nitrate. It forms dark reddish-brown crystals slightly soluble in cold, and rather more soluble in hot water.

The ferricyanides of most of the other heavy metals are precipitates, some of which, like that of tin, are colourless; but generally possessing a yellow, greenish-brown, or red-brown colour.

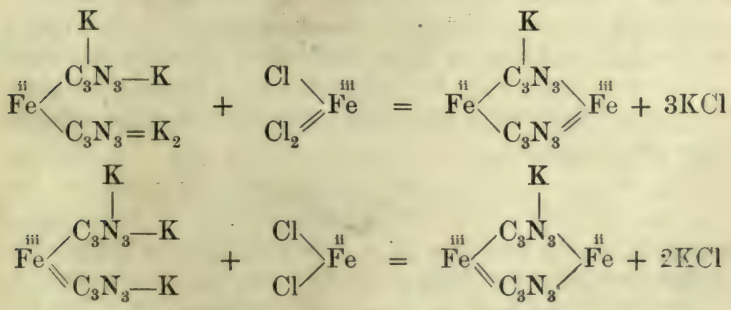
Ferrocyanides and Ferricyanides of Iron.

569 *Hydrogen Ferrous-Ferricyanide*, $Fe^{II}H_2[Fe(CN)_6]^{IV}$. This is a white powder obtained by boiling an aqueous solution of ferrocyanic acid (p. 1023). The corresponding potassium salt, $K_2Fe^{II}[Fe(CN)_6]^{IV}$, is found as a residue in the preparation of hydrocyanic acid from yellow prussiate of potash and dilute sulphuric acid, and the white precipitate produced by a ferrous salt in a solution of potassium ferrocyanide is probably the same substance. Both the foregoing compounds rapidly become blue coloured on exposure to the air from absorption of oxygen.

When the potassium salt is heated with dilute nitric acid the compound, $K\overset{iii}{Fe}[\overset{iv}{Fe}(CN)_6] + 2H_2O$, is obtained, which is known as Williamson's blue, and this, when dried, forms a fine violet-blue powder which is transparent when seen in thin layers, allowing green light to pass through. When it is heated with a solution of the ferrocyanide the white salt is again obtained, and the solution contains ferricyanide of potassium:[1]

$$K\overset{iii}{Fe}[\overset{iv}{Fe}(CN)_6] + K_4[\overset{iv}{Fe}(CN)_6] = K_2\overset{ii}{Fe}[\overset{iv}{Fe}(CN)_6] + K_3[\overset{iii}{Fe}(CN)_6]$$

Soluble Prussian Blue, Ferric Potassium Ferrocyanide, or *Ferrous Potassium Ferricyanide*, $KFe_2(CN)_6$. Ferric salts produce a blue precipitate in solutions of potassium ferrocyanide, which was formerly believed to be ferric ferrocyanide, and is sometimes, mistakenly, called Prussian blue. A precipitate very similar to this is obtained when solutions of potassium ferricyanide and ferrous sulphate are mixed. The precipitates thus obtained always contain potassium, and are stated to be in every respect identical; the precipitate possesses the same composition as the above-named violet-blue compound, but possesses different properties, and is obtained in the pure state by pouring solutions of the proper iron salts into an excess of ferrocyanide or ferricyanide The precipitate is then well washed with water in order to remove potassium chloride until the wash-water is coloured blue. The residue then consists of soluble Prussian blue. It is perfectly soluble in pure water, yielding a dark blue liquid from which it is precipitated by the addition of salts. The fact that ferric salts produce with a ferrocyanide solution a precipitate having the same composition as that which is formed when a ferrous salt is added to a ferricyanide solution is in agreement with Erlenmeyer's formulæ for the ferro- and ferri-cyanides.



[1] Williamson, *Mem. Chem. Soc.* 1846, 125.

The formulæ thus obtained are identical, inasmuch as it is immaterial which side of the compound contains the dyad ferrous, or the triad ferric group.[1] Soluble Prussian blue was first prepared from potassium ferrocyanide by Berzelius,[2] and Robiquet[3] observed that potassium forms an essential constituent, whilst Kekulé[4] was the first to propose the above formula. The truth of this, however, was proved by Reindel and Skraup, who showed that the precipitate obtained by ferricyanide and ferrous salt is identical with that obtained by ferrocyanide and ferric salt.

570 *Turnbull's Blue, Ferrous Ferricyanide, or Ferrosoferric Ferrocyanide,* $Fe_5(CN)_{12}$. This body was first prepared by Gmelin[5] by precipitating ferricyanide with ferrous sulphate. It was afterwards prepared on the large scale in England and named Turnbull's blue from the name of the supposed discoverer. Williamson[6] then showed that the precipitate thus obtained contains potassium, which can be removed by warming for some time with stannous chloride and subsequent washing with boiling water. The same compound is obtained by precipitating soluble Prussian blue with a ferrous salt, also by adding ferrous sulphate to a solution of ferricyanic acid (Reynolds),[7] and by precipitating a ferrocyanide with a mixture of a ferrous and ferric salt. On heating hydrocyanic acid is evolved and ferric oxide is formed, and when boiled with caustic potash, ferrocyanide of potassium and black ferroso-ferric hydroxide are formed:

$$Fe_5(CN)_{12} + 8KOH = 2K_4Fe(CN)_6 + Fe_3(OH)_8.$$

Ferric Ferrocyanide (*Insoluble Prussian Blue*), $Fe_4[\overset{IV}{Fe}(CN)_6]_3 = Fe_7(CN)_{18}$, is obtained, mixed with soluble Prussian blue, by pouring a solution of ferrocyanide of potassium or of ferrocyanic acid (Reynolds) into one of ferric chloride. By heating the precipitate for some time with ferric chloride the whole of the potassium may be removed. It is likewise obtained by oxidising Turnbull's blue with either nitric acid or chlorine water (Williamson):

$$6Fe_5(CN)_{12} + 3Cl_2 = 4Fe_7(CN)_{18} + 2FeCl_3.$$

[1] Skraup, *Annalen*, 1877, **186**, 371.
[2] *Schweigg. Journ.* **30**, 34.
[3] *Ann. Chim. Phys.* **44**, 279.
[4] *Lehrb. Org. Chem.* **1**, 327.
[5] *Schweigg. Journ.* **34**, 325.
[6] *Chem. Soc. Memoirs*, 1851, 125.
[7] *Journ. Chem. Soc.* 1887, i. 644.

This substance is also formed by precipitating soluble Prussian blue with ferric chloride (Skraup), and forms in the dry state a deep blue powder which, on trituration, assumes a bright copper-like lustre. It always contains a certain quantity of water which cannot be driven off by heat, as decomposition then takes place with evolution of hydrocyanic acid and formation of ferric oxide. When heated strongly in the air Prussian blue burns like tinder, and when warmed with caustic potash, ferrocyanide and ferric hydroxide are formed:

$$Fe_7(CN)_{18} + 12KOH = 3K_4Fe(CN)_6 + 4Fe(OH)_3.$$

Concentrated sulphuric acid converts it into a white pasty mass, neither hydrocyanic acid nor iron being removed. When this is dried in a vacuum on a porous plate an amorphous powder remains which is decomposed by water into Prussian blue and sulphuric acid (Berzelius).

Commercial Prussian blue is obtained by precipitating a solution of ferrous salt with ferrocyanide of potassium. The more or less deeply coloured precipitate is then exposed to the air and treated with chlorine water, dilute nitric acid, or bleaching powder solution, and afterwards with hydrochloric acid in order to remove ferric oxide which is formed. It is a deep blue powder or mass which, when dried, possesses a conchoidal fracture and copper-like lustre. It always contains more or less potassium, and is a mixture of the three preceding compounds in varying proportions. Prussian blue dissolves in ammonium tartrate with a violet colour, and in oxalic acid with a beautiful blue colour. This latter liquid was formerly much used as a blue ink. It has, however, now been replaced by the violet and blue aniline colours.

The several blue compounds of cyanogen and iron all contain water, and are hygroscopic, and a part of this water is so firmly combined, that it is only given off at a temperature at which the salt decomposes.

Prussian Green, $[Fe_3(CN)_8]_x$, is obtained as a green hydrated precipitate when an excess of chlorine is passed through a solution of ferro- or ferri-cyanide, the liquid then heated to boiling and the precipitate boiled with hydrochloric acid (Pelouze). When the dry compound is heated to 180° cyanogen gas is evolved and a violet-blue compound is formed. Caustic

potash decomposes Prussian green into ferric hydroxide and a mixture of potassium ferro- and ferricyanides:

$$3Fe_3(CN)_8 + 15KOH = 3K_4Fe(CN)_6 + K_3Fe(CN)_6 + 5Fe(OH)_3.$$

A green body, having probably the same composition as Prussian green, is obtained by the continued action of oxidising agents on Williamson's blue.

A third substance having the empirical formula $Fe_3(CN)_8$ is formed as a black mass when a saturated solution of potassium ferricyanide is heated with bromine. It is decomposed by potash into ferric hydroxide and potassium ferro- and ferri-cyanide, whilst on exposure to the air it passes into Prussian blue, with loss of hydrocyanic acid. It is probably to be regarded as a ferroso-ferric ferricyanide.[1]

A ferric salt of ferricyanic acid is not known in the solid state, for when ferric chloride is added to a solution of ferricyanide of potassium no precipitate occurs. The liquid, however, becomes of a dark-brown colour and probably contains the salt, $\overset{iii}{Fe}[Fe(CN)_6]$.

Potassium Carbonylferrocyanide, $K_3Fe(CO)(CN)_5 + 7H_2O$. When the violet precipitate obtained by adding ferric chloride to the mother liquor from the preparation of Prussian blue[2] is treated with potassium carbonate, potassium carbonylferrocyanide is obtained in rectangular tablets. Its solution gives an apple green precipitate with copper sulphate and a violet precipitate with ferric chloride. The corresponding acid, $H_3Fe(CO)(CN)_5$, and a number of salts have been prepared. These compounds are apparently formed from the ferrocyanides by the replacement of the group CNR^1 by CO.[3]

571 *Nitro-Prussides or Nitrosoferricyanides.* Leopold Gmelin and other chemists observed that the coffee-brown solution obtained by the action of nitric acid on yellow prussiate of potash yields a splendid purple-red colour in contact with sulphides of the alkalis. Playfair[4] showed in 1849 that this reaction is produced by the presence of a peculiar compound which is formed by the action of nitric acid upon the yellow or red prussiate. Nitro-prussic acid is obtained by passing nitric

[1] Reynolds, *Journ. Chem. Soc.* 1888, i. 767. [2] *Jahresber.* 1884, 1740.
[3] Muller, *Compt. Rend.* 1887, **104**, 994; *Ann. Chim. Phys.* 1889 (6), **17**, 93.
[4] *Phil. Trans.* 1849, ii. 477.

oxide into an acid solution of potassium ferrocyanide. Hydrogen ferricyanide is produced in the first instance:

$$4H_4Fe(CN)_6 + 2NO = 4H_3Fe(CN)_6 + 2H_2O + N_2,$$

and this acts on the nitric oxide as follows:

$$H_3Fe(CN)_6 + NO = H_2Fe(NO)(CN)_5 + HCN.$$

Potassium nitro-prusside is also produced when the precipitate formed by the action of a ferrous salt on potassium cyanide is treated with potassium nitrite:

$$KCN + 3Fe(CN)_2 + KNO_2 = K_2Fe(NO)(CN)_5 + FeO,$$

the ferrous oxide being finally converted into ferric oxide and ammonia being liberated.[1]

In order to prepare the nitro-prussides, powdered potassium ferrocyanide is treated with double its weight of strong nitric acid which has been previously mixed with an equal volume of water. The coffee-coloured solution evolves carbon dioxide, cyanogen, nitrogen, and hydrocyanic acid, and probably also cyanic acid, derived from the oxidation of the hydrocyanic acid. As soon as the whole is dissolved it is warmed on a water-bath, the evolution of gas continuing until the solution is not coloured blue by ferrous sulphate, but a dark green or grey precipitate falls down. On cooling, potassium nitrate crystallises out, from which the dark mother-liquor is poured off, saturated with sodium carbonate, and heated to the boiling point, when a green or brown precipitate is formed. This is removed by filtration, and the nitrates are again separated from the nitro-prussides by crystallisation. The solution can also be precipitated with sulphate of copper, and the bright green precipitate decomposed, after washing, by boiling with a soluble basic hydroxide and thus converted into soluble salts.

Sodium nitro-prusside is also formed when 34·5 g. of sodium nitrite, 15 g. sodium thiosulphate, and 41 g. potassium ferricyanide are boiled with 400 g. water, the liquid cooled and 120 g. sodium bisulphite solution (37° Baumé) added.[2]

The nitro-prussides may be regarded as ferricyanides, in which the group CNR[1] has been replaced by NO.

Nitroprussic acid, $H_2Fe(NO)(CN)_5$, is formed by decomposing the silver salt with hydrochloric acid, or the barium salt

[1] Städler, *Zeitsch. f. Chem.* 1869, **5**, 559.
[2] Prud'homme, *Journ. Chem. Soc.* 1891, ii. 410.

with dilute sulphuric acid. The red strongly acid solution leaves on evaporation in a vacuum dark-red deliquescent prismatic needles. This compound is very unstable and partially decomposes during the concentration of the liquid with formation of ferric hydroxide, hydrocyanic acid, &c.

Potassium Nitroprusside, $K_2Fe(NO)(CN)_5$, forms dark-red monosymmetric prisms which deliquesce in the air and are readily soluble in water.

Sodium Nitroprusside, $Na_2Fe(NO)(CN)_5+2H_2O$, crystallises most readily of all the nitroprussides, and is usually prepared by concentrating the solution as above described until a sufficient quantity of nitroprusside is crystallised out. This is then removed from the warm solution in order to avoid any admixture of nitrates. It is purified by crystallisation and forms large ruby-red rhombic prisms. It dissolves in 2·5 parts of water at 15° and is more soluble in hot water. When exposed to light, the solution decomposes with separation of Prussian blue and nitric oxide. Boiled with caustic soda ferrous hydroxide is separated, sodium ferrocyanide and sodium nitrite being formed:

$$6Na_2Fe(NO)(CN)_5+14NaOH=Fe(OH)_2 \\ +5Na_4Fe(CN)_6+6NaNO_2+6H_2O.$$

The nitroprussides of ammonium and of the alkaline-earth metals also form red, easily soluble salts, their solutions decomposing on standing or on boiling with separation of Prussian-blue and ferric oxide. The silver salt and the ferrous salt are flesh coloured precipitates.

The splendid purple colour which the nitroprussides impart to a solution of an alkaline sulphide is very characteristic, and this reaction is employed both for the detection of alkali sulphides and of small quantities of alkalis and alkaline earths in solution by passing a little sulphuretted hydrogen through the liquid in the latter case and then adding a few drops of nitroprusside solution. This purple compound is very unstable, decomposing quickly with formation of hydrocyanic acid, ammonia, nitrogen, ferrocyanides, ferricyanides, &c.

When alcoholic solutions of sodium sulphide and sodium nitroprusside are mixed this purple compound separates out in oily drops.

Iron Thiocyanates.

572 *Ferrous Thiocyanate*, $Fe(SCN)_2+3H_2O$, is obtained in large pale-green monosymmetric crystals by dissolving iron wire in concentrated thiocyanic acid and evaporating the liquid in absence of air. The salt dissolves readily in water, alcohol, and ether, and becomes red-coloured on exposure to the air.

Ferric Thiocyanate, $Fe(SCN)_3+3H_2O$. This compound is obtained in the pure state when a mixture in the right proportions of anhydrous ferric sulphate and potassium thiocyanate is treated with alcohol and the solution evaporated over sulphuric acid in a vacuum. Dark-red or almost black cubical crystals are deposited, and these dissolve readily in water, alcohol, and ether. If a concentrated aqueous solution be shaken with ether it becomes colourless and the ether attains a purple-red colour. On warming or diluting with water the deep red aqueous solution becomes colourless with deposition of ferric hydroxide. The solution is also decolorised in presence of reducing agents as well as on treatment with mercuric chloride or gold chloride, inasmuch as the double thiocyanates are formed which are deposited as black crystalline precipitates.

The reaction between a ferric salt and potassium thiocyanate in aqueous solution is not complete when equivalent quantities are employed, and the state of equilibrium which is produced in any mixture of the two depends on the degree of dilution, the temperature and the relative proportion of the two salts present.[1] When the deep red solution is diluted so as to be almost colourless and potassium thiocyanate then added, the deep red colour is again produced. Double salts with potassium thiocyanate, such as $Fe(CNS)_3.9KCNS+4H_2O$, $Fe(CNS)_3.3KCNS$ are obtained when solutions of ferric thiocyanate and the calculated amount of potassium thiocyanate are evaporated over sulphuric acid.

Iron and Silicon.

Silicides of Iron—Iron can be alloyed with silicon in all proportions up to about 30 per cent., and since silica and silicates are reduced by carbon in the presence of iron, all cast iron contains silicon, probably in the form of a silicide (p. 958).

[1] Krüss and Moraht, *Ber.* 1889, **22**, 2061; *Zeit. anorg.* 1891, **1**, 399; Magnanini, *Zeit. phys. Chem.* 1891, **8**, 1; Vernon, *Chem. News*, 1892, **66**, 177 *et seq.*; 1893, **67**, 66; Gladstone, *Chem. News*, 1893, **67**, 1.

The compound $SiFe_2$ is obtained by heating iron with silicon in the electric furnace, and forms magnetic prismatic crystals of sp. gr. 7. It is readily attacked by hydrofluoric acid.[1]

Compounds of the formulæ FeSi,$FeSi_2$ and Fe_3Si_2 have also been described.

Silicates of Iron.—Several ferrous and ferric silicates occur in the mineral kingdom, but they are more frequently found as double silicates, in which the alkali metals and the metals of the alkaline earths are present. These are generally isomorphous mixtures in which ferric oxide is replaced by alumina, whilst lime, magnesia, and the alkalis are substituted by ferrous oxide, manganous oxide, &c. For a description of these compounds works on mineralogy must be consulted.

The Iron Tree.—In Glauber's description of the preparation of *oleum martis* (see p. 1002) the following passage occurs:—"When such a red *massa* before it deliquesces to an *oleum* is laid in *oleum arenæ vel silicum* (the modern sodium silicate) for one or two hours, a tree grows out of it, with roots, stems, many branches, and twigs, wonderful to behold." This phenomenon depends upon the fact that water-glass, which always contains some carbonate, decomposes the ferric chloride into ferric silicate and basic ferric carbonate, whilst bubbles of carbon dioxide are given off, and thus filiform processes are produced. In place of the ferric chloride, ferrous chloride, cobalt chloride, nickel chloride, copper nitrate, and many other easily soluble metallic salts may be employed, and thus a series of differently coloured coral-like growths may be produced.

Detection and Estimation of Iron.

573 The ferrous salts, as has been stated, readily absorb oxygen, and their solutions, therefore, usually contain larger or smaller quantities of the ferric salts. Hence they give a bluish-white precipitate with ferrocyanide of potassium, and this on shaking with air assumes a dark-blue colour. Ferricyanide of potassium produces at once a dark-blue precipitate, whilst the ferric salts are coloured a dark-brown by this reagent, no precipitate being formed. By these reactions it is easy to ascertain whether a ferrous, or a ferric salt, or a mixture of both, is contained in solution.

[1] Moissan, *Compt. Rend.* 1895, **121**, 621.

With alkalis, ferrous salts give a white, or usually greenish precipitate which quickly changes to a dark-green colour on exposure to air, and afterwards becomes brown. Ferric salts give at once a brown precipitate. The presence of these latter may also be readily ascertained by the blood-red colour which they produce with soluble thiocyanates. A bead of microcosmic salt or borax is coloured dark green by ferrous salts. This colour readily changes to a yellow or reddish-brown by oxidation. On cooling, the colour becomes less distinct, disappearing altogether if only traces of ferric oxide are present. Iron can also be detected in the dry way by Bunsen's test. For this purpose the compound is heated on the end of a carbonised wooden match, which has previously been impregnated with fused sodium carbonate, held in the reduction zone of the non-luminous gas-flame. The whole is then rubbed up in an agate mortar with a little water, the particles of iron being extracted on the point of a magnetised knife-blade. The adhering particles of finely-divided iron are brought on to a small piece of filter paper, dissolved in a drop of aqua regia and a drop of potassium ferrocyanide added, this confirmatory test being necessary inasmuch as nickel and cobalt are also magnetic metals.

It has already been stated that manganese is obtained together with iron in the course of qualitative analysis, and the mode of their separation has already been described. The precipitate containing ferric hydroxide may also contain uranium. This is readily separated by digesting the precipitate with concentrated solution of ammonium carbonate. The washed residue is then dissolved in hydrochloric acid and the confirmatory test for iron applied.

The iron compounds do not impart any colour to the non-luminous gas-flame. The spectrum of the metal is extraordinarily rich in lines, more than 4,500 having been measured. A dark line in the solar spectrum corresponds to each of the bright lines in the visible part of the spectrum.

In the processes of *quantitative analysis* iron is determined both gravimetrically and volumetrically. In the first case the iron must be present as ferric salt. Ferrous salts are, therefore, previously oxidised by nitric acid and then precipitated by ammonia, the precipitate washed with boiling water, dried, ignited, and weighed as the sesquioxide. If the solution should contain tartaric acid, sugar, or other organic compounds,

ammonia produces no precipitate. In these cases the iron must be previously precipitated as sulphide; this is well washed, dissolved in nitric acid and the iron precipitated by ammonia, or the organic compound must be destroyed by ignition. If other metals precipitable by ammonia and sulphide of ammonium be present, the iron can be separated by adding sodium or ammonium acetate or succinate to the neutral solution and boiling, when basic ferric acetate or succinate is thrown down. This is filtered whilst hot, washed with boiling water, dried, and ignited, and weighed as ferric oxide. The precipitate may contain alumina, and this must then be separated by means of caustic potash.

The *volumetric determination* of iron is best carried out with ferrous salts. According to Marguerite's process, a standard solution of potassium permanganate is added to a solution of the ferrous salt containing free sulphuric acid. As soon as a permanent red coloration is noticed the oxidation is complete, and the quantity of iron is calculated from the following equation:

$$10FeSO_4 + 9H_2SO_4 + 2KMnO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 2KHSO_4 + 8H_2O.$$

In order to determine the strength of the permanganate solution recrystallised oxalic acid, pure iron wire, or pure ammonium ferrous sulphate, $FeSO_4 + (NH_4)_2SO_4 + 6H_2O$, is employed, seven parts by weight of the latter salt containing exactly one part of iron.

Penny's method depends upon the fact that a ferrous solution containing a free acid is oxidised to ferric salt by potassium dichromate as follows:

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O.$$

The completion of the reaction is ascertained by bringing a drop of the solution in contact with a very dilute solution of potassium ferricyanide on a porcelain plate, when no further blue colour should be observed. These volumetric methods are in daily use in iron-works for testing the value of the ore and for analysing the various products of the manufacture. As many of the ores of iron are ferric compounds they must be converted into ferrous salts. This is done by warming the acid

solution in a current of carbon dioxide in contact with pure zinc. In the laboratory the volumetric method is also frequently employed, as it not only is a quick and accurate method, but also because the amount of ferrous salt in the presence of ferric salt can thus be ascertained. For this purpose it is only necessary to treat the original solution with the standard permanganate, and afterwards to reduce another sample of the liquid with zinc. By this method likewise the tedious separation of alumina and ferric oxide may be avoided, inasmuch as both may be weighed together, then brought into solution, and this, after the reduction of the iron, treated by the volumetric method.

Marguerite's method does not give good results in the presence of hydrochloric acid, inasmuch as chlorine is in this case evolved. Hence if this acid be present it is either necessary to remove it by boiling with sulphuric acid, or Penny's method must be employed.

For other volumetric processes, for the volumetric estimation of ferric salts, and for the technical analysis of metallic iron, &c., works on analytical chemistry must be consulted.

The *atomic weight* of iron has been accurately determined by several chemists. Svanberg and Norlin,[1] by reducing the oxide in hydrogen obtained the number 55·67 as a mean of seven experiments. Berzelius found the number 55·58 as a mean of two experiments by oxidising the metal with nitric acid, and Erdmann and Marchand,[2] who reduced the oxide in hydrogen, obtained the number 55·58 as a mean of eight experiments. Maumené[3] dissolved pure iron wire in nitric acid and precipitated with ammonia, the mean of six experiments giving the number 55·58; and, lastly, Dumas,[4] by the analysis of ferric chloride, obtained the number 55·90, whilst by the analysis of ferrous chloride the number 55·56 was obtained. The most probable value is 55·6 (O = 15·88).

NICKEL, Ni = 58·4.

574 The first mention of an ore of this metal is found in the writings of Hiarni in 1694, under the name of kupfer-nickel, this name, signifying false copper, being given to it because,

[1] *Annalen*, 1844, **50**, 432.
[2] *Annalen*, 1844, **50**, 442.
[3] *J. pr. Chem.* 1844, **33**, 1.
[4] *Ann. Chim. Phys.* 1850 [3], **30**, 380.

whilst possessing the colour of a copper ore, this latter metal could not be extracted from it. In spite of the failure, the ore was long supposed to contain copper, but after the discovery of cobalt many believed that this metal was contained in kupfer-nickel.[1] In 1751 Cronstedt published in the *Transactions* of the Stockholm Academy an investigation upon an ore which was obtained from the mines of Helsingland. This gave a green vitriol, which imparted a brown and not a blue colour to glass, and yielded a hard brittle metal. In 1754 he stated that a semi-metal occurred most abundantly in kupfer-nickel, and therefore he proposed to give to it the name of nickel. He likewise showed that the speiss formed in the preparation of smalt consists to a large extent of nickel, and was not, as had been believed, a burnt cobalt which had lost its spirit. Cronstedt's views did not find general acceptance; but in 1774 Bergman's research on nickel made its appearance, and in this he showed that the nickel which Cronstedt had only obtained in the impure state was in reality a new metal.

Nickel almost always occurs in nature together with cobalt. Its most important ores are nickeline or kupfer-nickel, NiAs found in the Saxon mines, in Styria, at Leadhills, and in Connecticut; nickel-glance, NiAsS; breithauptite, NiSb; millerite or nickel-blende, NiS; linnaeite, $(Co,Ni,Fe)_3S_4$; pentlandite, (Ni,Fe)S; nickel-ochre or annabergite, $Ni_3(AsO_4)_2+8H_2O$; rewdanskite, $(Ni,Fe,Mg)_3Si_2O_7+2H_2O$, &c. Nickel also occurs frequently in magnetic pyrites, that from the Gap Mine in Pennsylvania containing 5·6 per cent., and being worked for nickel. An important source of nickel has been opened out in New Caledonia, where large quantities of a silicate of nickel called garnierite, $2(Ni,Mg)_5Si_4O_{13}+3H_2O$, occur; whilst a similar ore, containing about 2·56 per cent. of nickel and an equal amount of copper, is worked in Ontario, where it is sometimes accompanied by nickeliferous iron pyrites, $(Ni,Fe)S_2$. Similar ores also occur in Oregon.

Nickel is an essential constituent of meteoric iron (p. 936), its presence in extra-terrestrial matter having been first detected by Proust. It is also contained in the sun's atmosphere.

[1] See Link, *Phil. Trans.* 1726, 236.

Metallurgy of Nickel.

575 The preparation of metallic nickel from ores containing arsenic or sulphur is usually carried out in two stages, which consist in (1) the concentration of the nickel into a *speiss* or *matt* containing 40—70 per cent. of the metal, along with cobalt, copper, iron, arsenic, and sulphur; (2) the extraction of the nickel from this matt.

According to the older processes the ores are first roasted and then melted in blast furnaces with the addition of an appropriate material to form a slag with the oxide of iron, &c., formed by the oxidation of the ore. These operations are then repeated until the matt which is obtained contains the requisite amount of nickel.

When poor ores are being worked, such as those in Norway (2—4 per cent.), and in Canada (2—3 per cent.), the ore, which contains large amounts of iron and sulphur, is first roasted and then melted with lime and slag in a blast furnace. The mass thus prepared, containing 15—30 per cent. of nickel, is then treated in a converter with a blast of air, the process being similar to the Bessemer process for making steel (p. 974). The greater part of the arsenic, sulphur, and iron is thus removed by oxidation, and the resulting matt is found to contain in Norway, where the ores are free from copper, 75—77 per cent. of nickel and cobalt, and in Canada 40 per cent. of nickel and an equal amount of copper.

The concentrated matt may then be treated in either of several different ways.

The separation by the wet way is usually carried out by roasting the matt and treating the oxides thus formed with hydrochloric or sulphuric acid. The ferrous salts are then oxidised with bleaching powder, and the iron and arsenic precipitated by the addition of just sufficient lime or chalk, whilst the copper is afterwards thrown down with sulphuretted hydrogen or sodium sulphide. The cobalt is then precipitated by the requisite quantity of bleaching powder solution at 40°, and the nickel contained in the clear filtrate precipitated as the hydroxide or carbonate by milk of lime or soda ash. This is then ignited and purified by treatment with dilute hydrochloric acid, which dissolves the lime and calcium carbonate present, but does not attack the nickel oxide. Calcium

sulphate may, if present, be removed by heating the impure oxide with steam and adding soda ash solution in such quantity that after boiling for a quarter of an hour an excess still remains. The sodium sulphate is then removed by washing with water and the calcium carbonate (formed by double decomposition) dissolved in dilute hydrochloric acid. The metal is also sometimes deposited from solution by electrolysis.

The dry method, adopted in Canada, consists in roasting the matt and removing the copper, which is present to the extent of about 40 per cent., by chlorination and subsequent extraction of the copper chloride. The removal of iron is carried out in a reverberatory furnace, by a process similar to that used in the elimination of iron from the "coarse metal" in the metallurgy of copper (p. 309), and the residual nickel sulphide converted into the oxide by roasting.

The oxide is then pressed into the form of small cubes, and these strongly ignited with charcoal powder. The reduction takes place from the outside, the metal absorbing carbon and retaining the form of the cubes. The operation is usually carried on in clay crucibles standing on the hearth of a reverberatory furnace, or in a special furnace[1] which permits the reduction to be carried on continuously. This consists of a furnace through which vertical fire-clay tubes pass; these tubes are charged at the top with the mixture of crude oxide and coal, and the metal is withdrawn from time to time at the bottom. Commercial nickel contains carbon as well as small quantities of cobalt, copper, iron, zinc, and manganese.

The ore from New Caledonia, which is almost entirely free from cobalt, and contains no sulphur, may either be smelted in a blast furnace, fused with soda-ash, or worked up in the wet way by one of the following two processes; according to the first, the ore is treated with hydrochloric acid, and the solution precipitated with oxalic acid, and the insoluble oxalate reduced to metal by reduction with lime and carbon. Or the hydrochloric acid solution of the ore is heated with chalk to throw down iron and aluminium, and the nickel precipitated in the filtrate with a mixture of milk of lime and bleaching-powder.

An extremely interesting process has been introduced by Mond,[2] which depends on the formation of the volatile nickel carbonyl $Ni(CO)_4$ when the finely divided metal is exposed to the action of carbon monoxide at 80°. The Canadian matt is

[1] *Ber. Entw. Chem. Ind.* **1**, 866. [2] *Journ. Soc. Chem. Ind.* 1895, 945.

roasted and then exposed to the reducing action of water-gas or producer-gas at a temperature not exceeding 400°. The reduced metal is then passed by air-tight conveyers to the "volatiliser" in which it passes downwards over a series of shelves where it is exposed at a temperature of 80° to an ascending current of carbon monoxide. This gas is prepared by passing the flue gas from a boiler through potassium carbonate solution, boiling the solution, and leading the pure carbon dioxide given off over incandescent coke. The gas leaving the volatiliser contains nickel carbonyl and is passed through tubes or chambers heated to 180°, in which the nickel is deposited in the pure state, the carbon monoxide being regenerated and passing back to the volatiliser.

$$Ni(CO)_4 = Ni + 4CO.$$

Pure nickel can be prepared, according to Winkler,[1] by electrolysing a solution of the pure sulphate containing ammonium sulphate and ammonia, a cathode of highly polished nickel being used, and the current passed until the nickel separates from the electrode in thin plates. It is then heated in a current of pure dry hydrogen.

576 *Properties.*—Nickel is a lustrous silver-white metal having a steel-grey tinge. It is very hard and takes a fine polish, and may easily be rolled out into thin plates and drawn into wire. Its specific gravity is 8·9 and its specific heat at 50° is 0·1090. It is malleable and can be welded. When the metal contains carbon it is less malleable and more readily fusible than when pure. Nickel oxidises only with difficulty even on heating in the air, and melts at a somewhat lower temperature than iron and cobalt. It decomposes steam very slowly at a red-heat with formation of the monoxide, which is also formed when it is heated at 200° in nitric oxide.[2] It is soluble in hydrochloric or dilute sulphuric acid, and does not dissolve quickly even in the concentrated acid. On the other hand, it dissolves readily in dilute nitric acid; but if it be dipped into the concentrated acid it becomes "passive" as iron does. Nickel is attracted by the magnet and readily assumes a polar condition. It is capable of absorbing about 17 volumes of hydrogen. Nickel is now largely employed for plating and for the manufacture of alloys, among which nickel steel and German silver are the most important. The unalloyed metal, containing 98·7 per cent of

[1] *Zeit. anorg. Chem.* 1894, **8**, 1.

[2] Sabatier and Senderens, *Compt. Rend.* 1892, **114**, 1429.

nickel and cobalt, was adopted in 1892 by the Government of Austria-Hungary for the production of minor coins, and has been found to be very successful.[1] It is also employed for the manufacture of crucibles which can be used in many laboratory operations, instead of those made of the more costly platinum.

The amount of the metal produced in 1868 was only 700 tons, whereas after the opening of the Canadian mines in 1888 the production rapidly increased and in 1891 amounted to 4,500 tons.

Electro-nickel Plating.—Pure nickel is used as the positive pole in processes of the galvanic deposition of nickel which are especially valuable for coating iron and steel with a thin film of pure nickel. If the coating be well deposited it scarcely undergoes any oxidation, but it is found to adhere better when a layer of copper is first deposited on the iron. The process of nickel-plating was first applied to fire-arms in order to preserve them from rusting. Now, however, it is also used for covering various parts of machines, locks, keys, surgical instruments, and other fine iron- and steel-work, and is especially carried on in America. A great variety of proposals have been made for the preparation of the liquid used in this process, but the only bath which is practically useful is one made of pure nickel ammonium sulphate which is saturated at a temperature of from 20° to 25°.[2]

Alloys of Nickel.

577 In 1825 Thénard in his *Traité de Chimie* remarked that nickel was not employed for any practical purpose, although Engeström had pointed out so long ago as 1776 that Chinese packfong is an alloy of copper, zinc, and nickel. Packfong, or rather Pack-Tong, means white copper, and Tong-Pack probably means the same thing, although in Europe this name, changed to tomback, is employed to describe a particular kind of brass. Since the middle of the last century a white alloy has been prepared at Suhl, in Hanneberg, from old copper slag; and Brandes in 1823 showed that this white copper chiefly consists of an alloy of copper and nickel, and thus commenced the manufacture of nickel alloys known under the name of German-silver, nickel-silver, or argentan, a trade which has now attained large dimensions. The nickel industry received a further im-

[1] *Journ. Soc. Chem. Ind.* 1896, 455. [2] *Ber. Entw. Chem. Ind.* i. 874.

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pulse from the application of copper-nickel alloys to the manufacture of small coin, which was first introduced into Switzerland in 1850. The Swiss pieces of twenty, ten, and five centimes contain respectively fifteen, ten, and five per cent. of silver alloyed with 10 parts of nickel and 12·5 of zinc, the residue being made up of copper. These proportions are, however, not constant, as, in the melting, more or less zinc volatilises. A yellow alloy containing twelve of nickel to eighty-eight of copper was adopted in 1856 by the United States Government for the one cent pieces, and in 1860 the Belgian Government instituted a nickel-copper coinage, containing twenty-five of the former to seventy-five of the latter metal, this same alloy being adopted in 1866 by the United States for the five and ten cent pieces, by Brazil in 1872 and by the German Government in 1873 for the five- and ten-pfennig pieces.

The advantages of nickel coinage are, in the first place, that the metal is more valuable than copper, and, therefore, for the same value, the coins can be of smaller size; secondly, that the alloy is hard and, therefore, the coin wears well; thirdly, that the alloy requires experienced workmen to prepare in the homogeneous condition; and, lastly, that in consequence of its hardness it requires powerful machinery for its manufacture.

It is a very remarkable fact that a coin of the Bactrian King Euthydemos, who reigned about 235 before Christ, analysed by Flight[1] possesses a very similar composition to the alloy in question:

Copper	77·58
Nickel	20·04
Cobalt	0·54
Iron	1·05
Tin	0·04
Silver	trace
Sulphur	0·09
	99·34

The above alloys of nickel absorb on fusing a considerable quantity of gases, and the more the higher the temperature and the percentage of nickel contained. Künzel found that if an alloy of eighty parts of copper and twenty of nickel be fused in a crucible half filled with the mixture, and this quickly cooled

[1] The *Numismatic Chronicle*, **8**, 305; and *Pogg. Ann.* 1870, **139**, 507.

the mass froths up from the evolution of gas, and runs over the top of the crucible. If a copper nickel alloy be granulated in water, yellow globules are obtained, and these are frequently so thin that they swim on the surface of the water.[1]

Nickel-silver, or *German-silver* is an alloy of copper, nickel, and zinc, containing its constituents in varying proportions according to the method of preparation and the articles for which it is used. As a rule five parts of copper, two of nickel, and two of zinc are used, thus giving rise to an alloy which has the appearance of silver alloyed with one-quarter of copper. In Sheffield eight parts of copper, 3·5 of zinc, and three of nickel are employed. A commoner and yellowish alloy is obtained when less nickel is used, whereas if more nickel be employed the alloy has a bright white colour, and takes a high silvery polish. The addition of 2·5 per cent. of iron makes the alloy whiter, but also harder and more brittle.

The following table gives the composition of several of these alloys: No. I. is Chinese packfong analysed by Fyfe; II. the same, by Kefferstein; III. German-silver by Bolley; IV.—VI. various samples of nickel-silver used in Birmingham for articles to be plated, and analysed by Louyet; and VII. an alloy from Sheffield distinguished by extraordinary elasticity and used for the friskets of printing-presses, analysed by Elsner.

	I.	II.	III.	IV.	V.	VI.	VII.
Copper .	40·4	26·3	54·0	63·34	62·40	62·63	57·4
Zinc . .	25·4	36·8	28·0	17·01	22·15	26·05	25·0
Nickel .	31·6	36·8	18·0	19·13	15·05	10·85	13·0
Iron . .	2·6	—	—	trace	trace	trace	3·0
	100·0	99·9	100·0	99·48	99·60	99·53	98·4

In preparing nickel-silver it is usual to melt the zinc with half the weight of copper which it is ultimately to contain, this alloy being then cast into thin plates. The other half of the copper is then fused with the nickel under a bed of charcoal-powder, and the copper zinc alloy added. After cooling, the alloy possesses a crystalline structure, and this is got rid of by hammering and rolling, again heating, and allowing it to cool. When it has once lost its crystalline structure it can be worked like brass, and although it is harder and tougher it may be rolled out to foil and drawn to wire. Hence it is used for a

[1] *Ber. Entw. Chem. Ind.* i. 867.

great number of purposes, as it is much cheaper than silver, and less apt to be discoloured. On the other hand, it is more readily attacked by acid liquids, and for this reason nickel-silver articles employed for household use are generally covered with a coating of silver. The addition of small quantities of aluminium has recently been shown greatly to improve the quality and appearance of nickel silver.

An alloy of nickel with four parts of copper is used for the casing of bullets to be employed with small bore rifles.

Nickel-steel, containing 3—15 per cent. of nickel, is now largely used for armour plate and the construction of vessels. It is extremely tough, and has greater tensile strength than ordinary steel, whilst being equally ductile.

COMPOUNDS OF NICKEL.

Nickel and Oxygen.

578 Nickel only forms two well-defined oxides.

Nickel monoxide, NiO,
Nickel sesquioxide, Ni_2O_3.

In addition to these, trinickel tetroxide, Ni_3O_4,[1] has been described along with several other oxides, such as Ni_4O_7,[2] Ni_5O_7,[3] and Ni_3O_5,[4] the existence of which cannot be considered as established. The suboxides Ni_2O[5] and Ni_3O_2[6] have also been described, but it is doubtful whether they are not simply mixtures of nickel and the monoxide.

Of these oxides only the monoxide acts as a basic oxide forming a corresponding series of salts NiR'_2 when acted on by acids. Both the metal itself and all the oxides yield the monoxide when heated strongly in the air.

Although no oxide of the formula NiO_2 has been prepared, a salt of this oxide with baryta, barium nickelite $BaO,2NiO_2$ is known.

Nickel Monoxide, or *Nickel Oxide*, NiO. This substance

[1] Baubigny, *Compt. Rend.* 1878, **87**, 1082. Dudley, *Amer. Chem. Journ.* 1896, **18**, 901.
[2] Wicke, *Jahresber.* 1865, 303.
[3] Schröder, *Journ. Chem. Soc.* 1890, ii. 1213.
[4] *Chem. News*, 1879, **39**, 81.
[5] Müller, *Pogg. Ann.* 1869, **136**, 59.
[6] Moore, *Chem. News*, 1895, **71**, 81.

occurs as bunsenite at Johanngeorgenstadt in Saxony, in vitreous translucent pistachio-green regular octahedra having a specific gravity of 6·398. It may be obtained in the form of a green crystalline powder, which becomes deep yellow on heating, by strongly heating the hydroxide, sesquioxide, carbonate or nitrate. If nickel borate be ignited with lime in a pottery furnace and the mass treated with hydrochloric acid, nickel oxide remains behind in green cube-octahedra which have a specific gravity of 6·8 (Ebelmen), whilst if the metal be ignited in a current of steam, pale olive-green crystals of the oxide are formed. When heated in the air it at first absorbs oxygen, but loses it again at a higher temperature, whilst in the electric furnace it melts and solidifies in green crystals.[1] It is readily reduced by hydrogen at 220°, by carbon monoxide at 120°, and by solid carbon at 450°

Nickel Hydroxide, $Ni(OH)_2$, is thrown down when a solution of a nickel salt is heated with potash or soda, as an apple-green precipitate slightly soluble in water. It dissolves in ammonia with a blue colour, and separates out as a green crystalline powder on boiling the ammoniacal solution.

The salts of nickel are derived from the monoxide. In the anhydrous condition, and formed from colourless acids, they are usually yellow-coloured, whilst in the hydrated state they possess an apple-green to an emerald-green colour. The soluble normal salts have a slightly acid reaction and a sweetish astringent metallic taste and act as emetics.

Nickel Sesquioxide, Ni_2O_3, is a black powder obtained by gentle ignition of the nitrate or carbonate in the air, and is converted at a higher temperature into the monoxide. When the sesquioxide is heated in the oxy-coal-gas flame it yields metallic nickel,[2] which on cooling becomes covered with a film of oxide. It dissolves in sulphuric and nitric acids with evolution of oxygen, and in hydrochloric acid with evolution of chlorine, whilst nitrogen is evolved when it is acted upon by ammonia:

$$3Ni_2O_3 + 2NH_3 + 3H_2O = 6Ni(OH)_2 + N_2.$$

If chlorine be passed through the dihydroxide suspended in water, nickel trihydroxide, $Ni(OH)_3$, is obtained

$$3Ni(OH)_2 + Cl_2 = NiCl_2 + 2Ni(OH)_3.$$

[1] Moissan, *Ann. Chim. Phys.* 1880 (5), **21**, 199; *Compt. Rend.* 1892, **115**, 1034.

[2] Read, *Journ. Chem. Soc.* 1894, **1**, 314.

This compound is formed as a black precipitate when the solution of a nickel salt is warmed with an alkaline hypochlorite or hypobromite solution. On drying it forms a black mass with lustrous conchoidal fracture. Acids and ammonia act upon it as upon the sesquioxide.

Barium Nickelite, $BaO,2NiO_2$, is formed when barium carbonate is strongly heated with nickel sesquioxide in the electric furnace. It is thus obtained in dark-coloured crystals of specific gravity 4·8, which are rapidly decomposed by hot water and dissolve in hydrochloric acid with evolution of chlorine.[1]

Nickel and the Halogens.

579 *Nickel Fluoride*, NiF_2, is obtained by dissolving the hydroxide or carbonate in hydrofluoric acid, and evaporating, when blue-green crystals of NiF_2+3H_2O separate. These are decomposed by boiling water with formation of an insoluble pale green oxyfluoride.

The anhydrous fluoride is obtained by heating the chloride with ammonium fluoride in a current of hydrofluoric acid.[2] It forms volatile green prisms of specific gravity 4·63, which are not attacked by the mineral acids but are reduced by hydrogen.

Nickel fluoride forms double salts with the alkali fluorides.

Nickel Chloride, $NiCl_2$. Finely-divided nickel burns with a bright light when it is slightly heated in dry chlorine gas, forming yellow scales resembling Mosaic gold. If a solution of the oxide or carbonate in hydrochloric acid be evaporated to dryness the anhydrous chloride is obtained as a yellow earthy mass which readily dissolves in water with evolution of heat. On gently heating for some time in the air it evolves chlorine leaving a residue of the oxide. In absence of air, on the other hand, it can be sublimed, and is then obtained in golden scales which when boiled for some time with caustic potash are completely converted into the hydroxide. They become gradually coloured green on exposure to the air owing to the absorption of moisture, and are then easily soluble in water. The salt $NiCl_2+6H_2O$ is obtained in short six-sided prisms on concentrating the solution; these are easily soluble in water and in alcohol. The anhydrous chloride of nickel absorbs ammonia at the ordinary

[1] Dufau, *Compt. Rend.* 1896, **123**, 495.
[2] Poulenc, *Compt. Rend.* 1892, **114**, 1426.

temperature, swelling up to a white powder, possessing a slightly violet tinge, and having the composition $NiCl_2 6NH_3$. The same compound is obtained in blue octahedra by dissolving the chloride in ammonia and allowing the solution to cool. This salt readily evolves ammonia when exposed to the air. It is easily soluble in water, but less so in strong alcohol. Similar compounds are formed by the bromide and iodide.

Nickel Bromide, $NiBr_2$. Finely-divided nickel absorbs bromine vapour when heated in it, becoming incandescent. In absence of air, the bromide sublimes in golden scales which deliquesce on exposure. The solution, which is also obtained by bringing the metal in contact with bromine and water, gives on evaporation deliquescent needles of $NiBr_2 + 3H_2O$.

Nickel Iodide, NiI_2. If nickel powder reduced in hydrogen be heated with iodine, or if the hydroxide be dissolved in hydriodic acid, the solution evaporated to dryness in absence of air, and the solid heated, nickel iodide sublimes in iron-black scales. The solution when evaporated to a syrup deposits bluish-green very deliquescent prisms having the composition $NiI_2 + 6H_2O$.

Nickel and Sulphur.

580 *Nickel Monosulphide*, NiS, occurs as millerite, being occasionally found in brass-yellow rhombohedra, but more commonly in capillary crystals. When nickel and sulphur are heated together above the melting-point of the latter, this same compound is formed with incandescence as a bronze-yellow brittle mass which is not soluble in hydrochloric or sulphuric acid, but dissolves in nitric acid and aqua regia. The black hydrated sulphide is precipitated when ammonium sulphide is added to a nickel salt. This is difficultly soluble in hydrochloric acid, but slightly soluble with a brownish colour in ammonia, as well as in yellow sulphide of ammonium and other alkaline polysulphides, and is reprecipitated from these solutions on exposure to the air, or on addition of acetic acid. In the moist state it oxidises readily on exposure to the air. When a solution of a nickel salt is heated with sodium thiosulphate, the monosulphide is obtained in the form of a dense black precipitate which does not undergo alteration on exposure to the air, and which is not acted upon by boiling hydrochloric acid.

The sulphide is not precipitated by sulphuretted hydrogen in presence of dilute hydrochloric acid, and yet the precipitated sulphide, when obtained in alkaline solution, is found to be insoluble in dilute hydrochloric acid. It appears probable therefore that a rapid change of state occurs in the freshly precipitated sulphide, and that it thus passes into a form which is insoluble in dilute hydrochloric acid.

A *subsulphide*, Ni_2S, is said to be formed, together with nickel sulphide and a carbide of nickel, when metallic nickel is heated in carbon bisulphide vapour, and when nickel sulphate is heated with sulphur. It is only slowly attacked by acids.[1]

Linnaeite, $(Ni,Co,Fe)_3S_4$, forms pale steel-grey crystals belonging to the regular system, and also occurs in the massive state. It is an important nickel ore occurring at various places in considerable masses, especially in the mine of La Motte in Missouri. The ore there contains, according to Genth, about 30 per cent. of nickel.

Nickel Disulphide, NiS_2, is obtained as an impalpable iron-grey powder by strongly heating a mixture of nickel carbonate, potassium carbonate, and sulphur, the residue being lixiviated with water.

Nickel Sulphate, $NiSO_4$. This salt was first obtained in the pure and crystalline condition in 1775 by Bergman. In order to prepare it, nickel or its hydroxide or carbonate is dissolved in dilute sulphuric acid. When the solution contains an excess of acid and at the ordinary temperature, the salt, $NiSO_4 + 6H_2O$, separates in hard bluish-green quadratic pyramids. At a temperature of from 50° to 70° green monosymmetric crystals of the same composition separate out, and these become bluish and opaque when allowed to stand at the ordinary temperature. When the salt crystallises from aqueous solution at from 15° to 20°, green rhombic prisms isomorphous with magnesium sulphate, and having the composition $NiSO_4 + 7H_2O$, are deposited. This salt is also known as nickel vitriol, or morenosite, occurring in acicular crystals, and also as a fibrous efflorescence on certain nickel ores. Crystallised sulphate of nickel when heated to 100° leaves the salt $NiSO_4 + H_2O$ as a powder, and this loses the whole of its water above 280°, yielding the yellow anhydrous salt. One hundred parts of water dissolve (Tobler):

At	2°	16°	23°	41°	50°	60°	70°	
$NiSO_4$	30·4	37·4	41·0	49·1	52·0	57·2	61·9	parts.

[1] Gautier and Hallopeau, *Compt. Rend.* 1889, **108**, 1111.

The anhydrous sulphate absorbs ammonia, becoming strongly heated and increasing in bulk, forming a violet-white powder having the composition $NiSO_4.6NH_3$. On dissolving the sulphate in strong ammonia and cooling, or allowing it to evaporate over sulphuric acid, transparent dark-blue quadratic prisms crystallise out having the composition $NiSO_4.4NH_3 + 2H_2O$. A compound of the formula $2NiSO_4.10NH_3 + 7H_2O$ has also been described.

Nickel Ammonium Sulphate, $(NH_4)_2SO_4 + NiSO_4 + 6H_2O$. This salt is employed in the process of nickel-plating. It is obtained by dissolving nickel, free from iron and copper, in dilute sulphuric acid, and adding ammonium sulphate to the concentrated acid solution. The crystalline paste which is deposited is washed with cold water and purified by recrystallisation. It crystallises in short monosymmetric prisms. One hundred parts of water dissolve (Link):

	At	3·5°	16°	20°	30°	40°	50°	68°	85°	
$(NH_4)_2SO_4 + NiSO_4$		1·8	5·8	5·9	8·3	11·5	14·4	18·8	28·6	parts.

The salt is almost insoluble in an acidified solution of ammonium sulphate (Thomson). Many other double salts are known.

Nickel and the Elements of the Nitrogen Group.

581 *Nitronickel*, $Ni_2(NO_2)$, is formed as a black mass mixed with oxide when nitrogen peroxide is passed over reduced nickel, and in its properties resembles the corresponding cobalt compound (p. 1066).[1]

Nickel Nitrite, $Ni(NO_2)_2$, is obtained in solution by the decomposition of the sulphate with barium nitrite. It is a very unstable compound, but forms with potassium nitrite the easily soluble double salt $4KNO_2 + Ni(NO_2)_2$. This is obtained in brownish-red octahedra by mixing a concentrated solution of the nitrite with an excess of potassium nitrite. When potassium nitrite is added to a nickel solution containing a calcium salt, a yellow crystalline precipitate of $2KNO_2 + Ca(NO_2)_2 + Ni(NO_2)_2$ is formed, which possesses great similarity to potassium cobaltinitrite (see p. 1066), and if a solution contain a sufficient quantity of calcium together with nickel and cobalt,

[1] Sabatier and Senderens, *Bull. Soc. Chim.* 1893 (3), **9**, 669.

the whole of the nickel, as well as the cobalt, may be thrown down by potassium nitrite. This fact must be remembered in the separation of the two metals.

Nickel Nitrate, $Ni(NO_3)_2 + 6H_2O$, crystallises in green monosymmetric tables which dissolve in two parts of cold water and in alcohol, and effloresce on exposure to dry air, deliquescing however in moist air.

Phosphides of Nickel.—Phosphorus and nickel combine when heated together to form the compound P_2Ni_5, which also is obtained when nickel is fused together with phosphoric acid and charcoal powder. It is a silver-white, brittle, crystalline, non-magnetic mass which melts more readily than nickel. If the vapour of phosphorus be passed over red-hot nickel the compound P_2Ni_3 is obtained as a whitish-grey crystalline mass. Neither of these phosphides dissolve in hydrochloric acid, but they are readily soluble in nitric acid. If a solution of nickel chloride be added to a boiling solution of potash containing phosphorus, some tartaric acid being present in order to prevent the precipitation of the hydroxide, a black precipitate of Ni_2P is thrown down. This is slowly decomposed by hydrochloric acid, and readily by nitric acid (R. Schenk).

Arsenides of Nickel.—These two elements readily fuse together to form brittle alloys, some of which occur as minerals. Of these the most important is kupfer-nickel or nickeline, NiAs, which is found massive and also, although less frequently, crystallised in hexagonal pyramids. It has a light copper-red colour, and is an important ore of nickel, being found in various localities in Europe and America. Chloanthite, $(Ni,Co,Fe)As_2$, is another nickel arsenide occurring together with the preceding.

The Phosphates of Nickel are insoluble in water, and more or less soluble in the mineral acids. The *arsenates* possess similar properties, and some of them occur in the mineral kingdom.

Nickel and Boron.

582 *Nickel Boride*, NiB, is prepared in the electric furnace from its constituents, and forms brilliant prisms of specific gravity 7·39. It is decomposed by fused alkalis and by water vapour at a dull red heat.[1]

[1] Moissan, *Compt. Rend.* 1896, **122**, 424.

Nickel and the Elements of the Carbon Group.

583 *Nickel Tetracarbonyl*, $Ni(CO)_4$. When carbon monoxide is passed over metallic nickel at about 350–400°, carbonic acid gas is formed and carbon liberated, but at a lower temperature the metal unites with carbon monoxide to form nickel tetracarbonyl. This substance is best prepared by reducing nickel oxide in hydrogen at about 400° in a combustion tube, allowing it to cool to about 30—80°, and then passing carbon monoxide over the reduced metal. When the issuing gas is cooled by salt and ice it deposits the nickel carbonyl, the excess of the gas being again passed over the nickel, and this repeated until no more of the compound is formed. The metal is then again heated in hydrogen to 400°, cooled and treated with carbon monoxide, the whole process being repeated as often as desired; about 10—15 grams are obtained at each operation.[1]

Nickel tetracarbonyl is a colourless liquid, which boils at 43°, has the specific gravity 1·3185 at 17°, and solidifies at −25°, forming needle-shaped crystals. It has the normal vapour density of 6·01 at 50°, but the vapour explodes at 60°, some carbon dioxide being formed and carbon liberated. When the vapour mixed with some indifferent gas (hydrogen or nitrogen) is passed through a tube heated to 180°, pure metallic nickel is deposited and carbon monoxide liberated according to the equation:

$$Ni(CO)_4 = Ni + 4CO.$$

The liquid is soluble in alcohol, benzene, and chloroform, and is not acted on by dilute acids or alkalis, or by water free from air, whilst concentrated nitric acid readily oxidises it, and on exposure to water and air, nickel hydroxide is formed along with a white compound of unknown constitution, which contains carbon.[2] The vapour of the liquid burns in the air with an intensely luminous flame, the spectrum of which is continuous.

Cobalt does not appear to form an analogous compound, so that nickel can readily be obtained absolutely free from cobalt by this reaction. The formation and subsequent decomposition by heat of this substance has also been made the basis of a process for extracting nickel from its ores (p. 1042).

[1] Mond, Langer and Quincke, *Journ. Chem. Soc.* 1890, i. 749.
[2] Berthelot, *Compt. Rend.* 1891, **112**, 1343; **113**, 679.

The vapour is poisonous, symptoms of carbon monoxide poisoning being produced.

Nickel Carbonate, $NiCO_3$, is obtained in the form of pale-green microscopic rhombohedra, by heating nickel chloride solution with calcium carbonate to 150°. When a nickel nitrate solution is mixed with solution of sodium bicarbonate saturated with carbon dioxide, and this allowed to stand at a low winter temperature, microscopic monosymmetric crystals of $NiCO_3+6H_2O$ are formed, and these lose their water readily on warming. When a nickel solution is precipitated with an alkali carbonate, basic salts of varying composition are thrown down in the form of pale-green precipitates.

Nickel Cyanide, $Ni(CN)_2$, is an apple-green precipitate easily soluble in an excess of potassium cyanide with formation of the crystalline double salt, $Ni(CN)_2+2KCN$. This is again decomposed by dilute acids with separation of nickel cyanide. No stable salts corresponding to the ferro- and ferri-cyanides are formed.

Nickel Silicide, Ni_2Si, is obtained by heating an excess of nickel with silicon in the electric furnace until the greater part of the metal has been volatilised, and then treating the residue with dilute nitric acid. It is a steel-grey crystalline powder with a metallic appearance, and has the specific gravity 7·2. It is readily attacked by fluorine, and dissolves in hydrofluoric acid and in aqua regia.[1]

The Nickel Silicates occur in nature. Rewdanskite occurs at Rewdansk in the Urals, and is worked for nickel. It is an earthy mineral which chiefly consists of $(Ni,Fe,Mg)_3Si_2O_7+2H_2O$, and contains about 18 per cent. of nickel. Garnierite, $2(Ni,Mg)_5Si_4O_{13}+3H_2O$, occurs in New Caledonia, and is now largely worked up for nickel in France. It contains 24 per cent. of nickel (Liversidge).

The *orthosilicate*, Ni_2SiO_4, is formed in greenish-yellow crystals when the oxide and chloride are heated with amor hous silica.[2]

Detection and Estimation of Nickel.

584 Nickel compounds behave in a similar manner to those of iron and cobalt when heated with reducing agents before the blowpipe. An infusible magnetic powder is produced, and

[1] Vigouroux, *Compt. Rend.* 1895, **121**, 686.
[2] Bourgeois, *Compt. Rend.* 1889, **108**, 1177.

when this is dissolved in a drop or two of dilute nitric acid and evaporated to complete dryness, a characteristic green stain is obtained which becomes yellow on further heating. Nickel compounds, moreover, colour the borax bead a brownish-yellow in the oxidising flame, the bead becoming grey and opaque in the reducing flame owing to the separation of metallic nickel.

Nickel is precipitated in alkaline solution by ammonium sulphide along with the other metals of the iron group, from all of which except cobalt it can be separated by treating the precipitate with dilute hydrochloric acid, in which the sulphides of these two metals are insoluble. The separation from cobalt is described under the latter metal. A characteristic property of nickel sulphide is that it dissolves in yellow ammonium sulphide, forming a dark-coloured solution.

Nickel is usually estimated as the oxide, the carbonate or hydroxide being precipitated and then ignited. It may also be deposited by the electrolytic method and weighed as the metal.

The nickel compounds give no flame-spectrum, but the chloride yields a characteristic spark-spectrum, and the spectrum of the metal also contains many lines, of which a few of the brightest are:

In the orange	5893
In the green-blue	4874 4866 4856

The atomic weight of nickel has been frequently determined, but with somewhat discordant results. Of the older determinations the most important are those of Russell[1] (1862), who in a series of well-agreeing experiments obtained the number 58·30, by reducing the strongly ignited monoxide, whilst by measuring the amount of hydrogen evolved on dissolving the pure metal he got the number 58·27.[2] On the other hand, Schneider[3] by analysing the oxalate found the numbers 57·63, and Dumas[4] by the analysis of the chloride obtained an atomic weight of 58·60, whilst Zimmermann, adopting the method used by Russell of reducing the pure oxide, more recently obtained the number 58·27.[5] In 1867 Winkler obtained the

[1] *Journ. Chem. Soc.* 1863, 58.
[2] *Journ. Chem. Soc.* 1869, 292.
[3] *Pogg. Ann.* 1857, **101**, 387.
[4] *Ann. Chim. Phys.* 1859 (3), **55**, 129.
[5] *Annalen*, 1885, **232**, 324.

number 58·83 by the precipitation of gold by metallic nickel.[1] This method was afterwards found to be inaccurate,[2] and Winkler has since obtained the numbers 58·60 by the analysis of nickel chloride,[3] and 58·42 from a very carefully conducted series of experiments,[4] in which pure nickel (p. 1043) was dissolved in an excess of pure iodine and potassium iodide solution, the excess of iodine being estimated by means of sodium thiosulphate. This last result, 58·47, probably represents the most reliable value for the atomic weight of nickel (O = 15·88). The statement made by Krüss and Schmidt[5] that ordinary "pure" nickel contains another element has not been confirmed.

COBALT. Co = 59.

585 The word cobalt occurs in the writings of Paracelsus and Agricola as well as in those of "Basil Valentine"; two meanings were attached to this name; in the first place it signified a sprite or goblin supposed to haunt the mine, whilst in the second place it was used to denote certain minerals, which are, however, too imperfectly described for exact identification. But it appears that in this latter sense it was employed to designate minerals which, although they possessed the appearance of a well-known metallic ore, did not yield any of this metal when subjected to the usual treatment. Hence the word came to signify a false ore. In later times the same name was given to the mineral which was used for the purpose of colouring glass blue, and is still employed for the preparation of smalt. In 1735, Brandt stated that the blue colouring of smalt depends upon the presence of a peculiar metal to which he gave the name kobalt-rex, and in 1742 he showed that the colour of smalt does not depend, as had been believed, upon the presence of arsenic and iron, metals which are usually found in cobalt ores, for he found that some of these ores occur free from arsenic, and that these likewise give the blue colour. The new metal was stated to be magnetic and extremely infusible. These observations were confirmed by Bergman in 1780, and

[1] *Zeit. anal. Chem.* 1867, **6**, 22.

[2] Krüss and Schmidt, *Ber.* 1889, **22**, 11; Winkler, *Zeit. anorg. Chem.* 1894, **8**, 12.

[3] *Zeit. anorg. Chem.* 1893, **4**, 10.

[4] *Zeit. anorg. Chem.* 1895, **8**, 1.

[5] *Ber.* 1889, **22**, 11; *Zeit. anorg. Chem.* 1893, **2**, 235.

the compounds of cobalt were afterwards examined by many chemists.

Cobalt does not occur in the free state in nature, and its ores, in which it is usually accompanied by nickel, are not very widely distributed. It is found as linnaeite Co_3S_4; skutterudite $CoAs_3$; speiss-cobalt $(Co,Ni,Fe)As_2$; glance-cobalt (Co,Fe)AsS; earthy cobalt, or wad $(Co,Mn)O,2MnO_2+4H_2O$; erythrine, or cobalt-bloom $Co_3(AsO_4)_2+8H_2O$, &c.

Cobalt is likewise almost always found as a constituent of meteoric iron, and its presence has been detected in the solar atmosphere.

Treatment of Cobalt Ores. For the preparation of cobalt compounds speiss-cobalt or other arsenical ores are employed. These, after roasting or calcination in the air, yield an impure cobalt arsenate which comes into commerce under the name of *zaffre*, and which is further worked up as hereafter described. The cobalt ores, however, usually contain large quantities of nickel and iron as well as other metals, and for this reason they are usually smelted in order to get rid of the greater part of the iron, the process employed being similar to that which is used for the extraction of copper. The roasted ore is fused with a flux of calcium carbonate or sand, when the iron slag flows on to the surface whilst the cobalt remains below as a heavy *speiss* or stone. The roasted ore or the speiss is then dissolved in strong hydrochloric acid, any arsenate of iron which may be present being precipitated by the careful addition of bleaching-powder solution and a small quantity of milk of lime; the clear supernatant liquid is drawn off, treated with sulphuretted hydrogen for the purpose of separating copper, bismuth, &c., and the oxide of cobalt then precipitated from the clarified solution by bleaching-powder. The oxide thus obtained is washed and ignited, and this is brought into the market and largely used for colouring glass and porcelain as well as for the preparation of the chloride and nitrate of cobalt. This oxide usually contains iron and almost always nickel and other impurities. A large amount of cobalt oxide is extracted from the manganiferous brown iron ores of New Caledonia, which contain about 2 per cent. of cobalt and an equal amount of nickel.

The extraction of cobalt from nickel ores has already been described.

586 *Preparation of Metallic Cobalt.* The metal is obtained

as a grey powder by igniting the oxide or chloride in a current of dry hydrogen. By strongly heating the oxalate under a layer of powdered glass the metal can be obtained as a coherent mass, and this may be fused to a regulus by heating it in a crucible made of lime, magnesia, or graphite. Cobalt possesses the colour of polished iron; it is, however, harder than this metal, although it melts at a somewhat lower temperature. It is malleable and very tough; it is also magnetic and has a specific gravity varying from 8·5 to 8·7. Cobalt in the form of powder absorbs oxygen from the air, often with ignition; the compact metal, however, does not undergo change at the ordinary temperature, but slowly oxidises when heated and burns at a very high temperature with a red flame. The metal also burns at 150° in nitric oxide, forming the monoxide.[1] It is capable of absorbing 59—153 volumes of hydrogen. The metal is readily soluble in hydrochloric, dilute sulphuric, and nitric acids, and, at a red heat, decomposes steam.

Pure cobalt does not become passive when immersed in nitric acid, and in this respect differs from nickel and iron.[2] It combines with silicon and boron to form crystalline compounds which resemble the corresponding nickel compounds, and are obtained in a similar manner (pp. 1053, 1055).

Pure cobalt may be obtained, according to Winkler,[3] by electrolysing a solution of pure cobalt sulphate in presence of ammonium sulphate and ammonia, platinum electrodes being used. The metal thus deposited invariably contains a small amount of oxygen (0·2—0·3 per cent.), and must therefore be heated in pure hydrogen.

COMPOUNDS OF COBALT.

Cobalt and Oxygen.

587 Cobalt forms three well-defined oxides:

Cobalt monoxide, CoO.
Cobalt sesquioxide, Co_2O_3.
Tricobalt tetroxide, Co_3O_4.

In addition to these the dioxide, CoO_2, probably exists, and

[1] Sabatier and Senderens, *Compt. Rend.* 1892, **114**, 1429.
[2] Sant-Edme, *Compt. Rend.* 1889, **109**, 304.
[3] *Zeit. anorg. Chem.* 1895, **8**, 1.

several others such as Co_8O_9,[1] Co_6O_7[2] and Co_4O_5,[3] Co_3O_5 [4] have been described.

Of these oxides, the first, CoO, is a well-marked basic oxide, corresponding to the stable cobaltous salts in which the metal is divalent. The sesquioxide acts as a feebly basic oxide, and the corresponding salts are unstable and are easily reduced to cobaltous salts. The dioxide appears to have a decided acidic function, and forms cobaltous acid, H_2CoO_3, which is only known in solution, although several stable cobaltites are known.

Cobalt Monoxide, or Cobaltous Oxide, CoO. This compound is obtained by reducing the higher oxide by heating it either in a current of hydrogen to a temperature not above 350° (Winkelblech) or in a current of carbon dioxide to redness until its weight is constant (Russell).[5] It is a light-brown powder, which does not alter in the air at the ordinary temperature, but when heated yields tricobalt tetroxide, Co_3O_4. When heated in the electric furnace, it melts and yields rose-coloured needles.

Cobaltous Hydroxide, $Co(OH)_2$, is obtained by precipitating a cobaltous salt with caustic potash in the absence of air. A blue basic salt is first obtained, and this, on boiling, is quickly converted into a rose-red-coloured hydroxide. It absorbs oxygen from the air and changes to a brown tint and dissolves in hot very concentrated potash, crystallising out on cooling in microscopic prisms.[6]

The cobaltous salts may be prepared by the action of acids on cobaltous hydroxide. They are the most stable of the cobalt salts, but undergo oxidation more readily than the corresponding compounds of nickel. In the anhydrous state they possess a deep violet or blue colour, and in the hydrated condition a faint rose-red tint.

Cobaltic Oxide or Cobalt Sesquioxide, Co_2O_3, is a dark-brown powder formed by gently igniting the nitrate.

Cobaltic Hydroxide, $Co(OH)_3$, is prepared by precipitating a cobalt salt with an alkaline hypochlorite solution. The composition of this precipitate depends on the conditions under which it has been produced, and it frequently, especially when prepared

[1] *Zeit. anal. Chem.* 1868, **7**, 336; *J. pr. Chem.* 1856, **69**, 131.
[2] *Pogg. Ann.* 1847, **61**, 472; 1852, **84**, 560.
[3] *Jahresber.* 1868, 265.
[4] *Journ. Chem. Soc.* 1890, ii. 1213.
[5] *Journ. Chem. Soc.* 1863, 51.
[6] Schulten, *Compt. Rend.* 1889, **109**, 266.

in the cold, contains more oxygen than corresponds to the formula Co_2O_3.[1] It forms a brownish-black powder, which is decomposed by hydrochloric acid with evolution of chlorine, and by oxy-acids with evolution of oxygen.

The sesquioxide and its hydroxide act, therefore, as peroxides, but at the same time they possess weak basic properties, inasmuch as they dissolve in well-cooled acids with a brownish-yellow colour. One of the most stable of these compounds is a strongly coloured solution obtained by dissolving the hydroxide in acetic acid; this decomposes only when heated. The corresponding sulphate and some of its double salts have however been isolated in the crystalline form.

Tricobalt Tetroxide or Cobalto-Cobaltic Oxide, Co_3O_4. This compound, which corresponds to the magnetic oxide of iron, is obtained when one of the other oxides or the nitrate is heated in the air; thus obtained, it forms a black powder having a specific gravity of about 6·0. If a dry mixture of sal-ammoniac and cobalt oxalate or cobalt chloride be heated in the air, or in oxygen, this compound is obtained in hard, metallic-lustrous, microscopic octahedra, which are not magnetic. It is obtained in the hydrated state by the oxidation of moist cobaltous hydroxide in the air. When heated in the oxy-coal gas flame it yields metallic cobalt, which becomes covered with a film of oxide as it cools.[2] The substance obtained by fusing one of the oxides with caustic potash, which was thought to be potassium cobaltate,[3] $Co_9O_{16}K_2 + 3H_2O$, is probably simply cobalto-cobaltic oxide contaminated with potash.[4]

Cobalt Dioxide, CoO_2, has not been obtained in the pure state. It appears, however, to be formed as a greenish-black precipitate when iodine and caustic soda are added to a solution of a cobaltous salt.[5] An oxide approaching this in composition is also formed by the action of a hypochlorite on a cobaltous salt, and is probably instrumental in bringing about the well-known evolution of oxygen which occurs when bleaching powder solution is warmed with a small quantity of a cobalt salt (vol. i. 220).[6]

[1] Carnot, *Compt. Rend.* 1889, **108**, 610; Schröder, *Journ. Chem. Soc.* 1890, ii. 1213.

[2] Read, *Journ. Chem. Soc.* 1894, i. 314.

[3] Schwarzenberg, *Annalen*, 1856, **97**, 212; Pebal, *Annalen*, 1856, **100**, 257; Mayer, *Annalen*, 1857, **101**, 266.

[4] McConnell and Hanes, *Journ. Chem. Soc.* 1897, **1**, 584.

[5] Vortmann, *Ber.* 1891, **24**, 2744. [6] McLeod, *British Assoc.* 1892, 669.

Cobaltous Acid, H_2CoO_3. When cobaltous hydroxide is suspended in water and treated with hydrogen peroxide, and the liquid filtered, a strongly acid colourless filtrate is obtained which appears to contain cobaltous acid. If potassium bicarbonate be added to this filtrate, or if the oxidation be carried out in presence of potassium bicarbonate, a green solution is obtained, which probably contains potassium cobaltite, K_2CoO_3. Sulphuric and sulphurous acids decolorise the green solution, but the colour reappears on neutralisation with potassium bicarbonate. Acetic acid does not decolorise the liquid, whilst, on warming with sulphuric acid, a pink solution of cobaltous sulphate is obtained.[1]

Barium cobaltite, $BaO.CoO_2$, and *acid barium cobaltite*, $BaO.2CoO_2$, are formed in black crystals when cobalt sesquioxide is fused with baryta and barium chloride.[2] These compounds evolve chlorine when treated with hydrochloric acid.

Magnesium cobaltite, $MgO.CoO_2$, is formed as a deep garnet-red mass when magnesia is fused with cobalt sesquioxide in the electric furnace.[3]

Cobalt and the Halogens.

588 *Cobalt Fluoride*, CoF_2, is obtained by dissolving the oxide or carbonate in hydrofluoric acid; on evaporation rose-red crystals are deposited having the composition $CoF_2 + 2H_2O$: these are decomposed by boiling water with the formation of a light-red insoluble oxy-fluoride.

The anhydrous fluoride is prepared in a similar manner to the nickel salt (p. 1049), and forms rose-coloured prisms which are slightly soluble in water.[4]

It forms double salts with the alkali fluorides.

Cobalt Chloride, $CoCl_2$. Powdered metallic cobalt takes fire when warmed in chlorine gas, forming blue crystalline scales of the anhydrous chloride, which can be readily sublimed in a current of chlorine. They dissolve in alcohol with a blue colour and on addition of water first become violet, and then rose-

[1] McConnell and Hanes, *Journ. Chem. Soc.* 1897, **1**, 584; compare Durrant, *Proc. Chem. Soc.* 1895-6, **96**, 244.

[2] Rousseau, *Compt. Rend.* 1889, **109**, 64.

[3] Dufau, *Compt. Rend.* 1896, **123**, 239.

[4] Poulenc, *Compt. Rend.* 1892, **114**, 1426.

coloured. Cobalt chloride is obtained in aqueous solution by dissolving the carbonate, or one of the oxides, in hydrochloric acid; short dark-red monosymmetric prisms crystallise on cooling the concentrated warm solution; these possess the composition $CoCl_2 + 6H_2O$ and have a specific gravity of 1·84. When these crystals are allowed to stand over sulphuric acid at 50° the violet rose-coloured dihydrate, $CoCl_2 + 2H_2O$, is formed, and when heated to 100° the deep violet monohydrate remains, which at 110—120° yields the blue anhydrous chloride. A strong aqueous solution is rose-coloured, but becomes blue when it is heated and when concentrated hydrochloric or sulphuric acid or alcohol is added. The rose colour is restored when the chlorides of zinc, mercury, antimony, or tin are added to the solution which has been rendered blue by hydrochloric acid. According to Engel[1] the change of colour is due in every case to the formation of double compounds, whereas Potilitzin,[2] Etard,[3] and others ascribe it to the formation of different hydrates.

An unstable compound, $CoCl_2.HCl + 3H_2O$, separates in blue crystals at −23° from a saturated solution of cobalt chloride in hydrochloric acid. A corresponding lithium compound is known, which is also blue.[4]

Sympathetic Inks. If a dilute solution of the chloride be used as an ink the writing is not visible when it is allowed to dry in the air, but, on warming, the characters appear of a bright blue colour, disappearing again gradually on standing in the air owing to the absorption of moisture.

From this property the cobalt salts have long been employed for the manufacture of the so-called *sympathetic inks*, by which is understood any liquid the writing of which is invisible under ordinary conditions but which can be rendered apparent by some simple treatment. The first attempt at the preparation of such an ink depended upon the fact that a solution of lead acetate becomes black when treated with a decoction of orpiment in milk of lime. These two liquids, which were known as "aquæ magneticæ e longinquo agentes," were mentioned by Lemery in 1681 as "encres appellées sympathiques." Soon after this other sympathetic inks were made known in the treatise termed *The Key to unlock the Cabinet of the Secrets of*

[1] *Bull. Soc. Chim.* 1891 (3), **6**, 239. [2] *Bull. Soc. Chim.* 1891 (3), **6**, 264,
[3] *Compt. Rend.* 1891, **113**, 699; see also Charpy, *Compt. Rend.* 1891, **113**, 794; and Sabatier, *Compt. Rend.* 1888, **107**, 42.
[4] Chassevant, *Ann. Chim. Phys.* 1893 (6), **30**, 5.

Nature, published in 1705; and the method for preparing a sympathetic ink from certain bismuth ores is described. Up to the year 1744 the peculiar properties of this ink were believed to be due to bismuth, but in that year Gessner proved that the cobalt contained in these ores was the active agent in the production of the ink. This property of the cobalt salts to change colour from rose to blue on loss of water has also been applied to the construction of floral hygrometers. Artificial flowers are prepared, the petals of which are tinted with cobalt salts. In damp weather the flower is pink, in dry weather violet or blue. This invention is, we need scarcely add, a Parisian one.

Cobalt Bromide, $CoBr_2$. If bromine vapour be passed over metallic cobalt at a dark red-heat, a green fused mass is formed which absorbs water from the air, yielding a dark-red liquid. This solution is also obtained by bringing cobalt, bromine and water together; if the solution be allowed to stand over sulphuric acid, dark red prisms having the composition $CoBr_2 + 6H_2O$ are deposited, and these when heated to 100° give a purple mass containing $CoBr_2 + 2H_2O$, which at 130° yields the anhydrous bromide as an amorphous green mass (Rammelsberg, Hartley).

Cobalt Iodide, CoI_2. This substance is formed with evolution of heat when finely divided cobalt is gently warmed with water and iodine. The saturated solution is red up to 20°, and then passes through brown and olive to green at 35°. When poured into a saturated solution of magnesium chloride a blue solution is formed (Etard). The hydrate $CoI_2 + 6H_2O$ is dark red, whilst the tetrahydrate and the dihydrate are green, and the anhydrous salt resembles iodine.

Cobalt and Sulphur.

589 *Cobalt Monosulphide*, CoS, is obtained as a black hydrated precipitate when a solution of a cobalt salt is mixed with ammonium sulphide. It dissolves in concentrated hydrochloric acid with evolution of sulphuretted hydrogen. The cold dilute acid dissolves it but slowly, whilst it is almost insoluble in dilute acetic acid. When the monosulphide is mixed with sulphur and the mixture ignited in a current of hydrogen the following sulphides are formed according to the temperature employed: CoS_2, Co_2S_3, CoS; and at a white heat, Co_2S (H. Rose). The

monosulphide is found as an Indian mineral known as syepoorite, occurring in ancient schists in grains or veins of a yellowish steel-grey colour.

Cobalt pyrites or linnaeite, Co_3S_4, occurs at Bastnäs, near Riddarhyttan, at Müssen in Prussia, as well as at Mineral Hill in Maryland, and at Mine La Motte in Missouri. It forms steel-grey or tarnished copper-red regular octahedra, and also occurs in the massive state. It usually contains more or less nickel as well as some iron and copper. The same compound can be artificially obtained as a blackish-grey powder by heating a solution of a cobalt salt with potassium polysulphide to a temperature of 160°.

Cobaltous Sulphite, $CoSO_3+5H_2O$, is a pink crystalline powder.

Cobaltic Sulphite has not been isolated, but several double compounds, which are probably salts of a complex cobaltisulphurous acid, $H_3[Co^{III}(SO_3)_3]$ have been described.[1]

Cobaltous Sulphate, $CoSO_4+7H_2O$. This salt occurs native as cobalt vitriol, or bieberite, in crystalline crusts. It is prepared artificially by dissolving the carbonate or oxides in dilute sulphuric acid, and crystallises in red prisms having the form of iron vitriol, which are unalterable in the air. It has a specific gravity of 1·924 (Schiff), possesses a weak astringent metallic taste, is easily soluble in water, but does not dissolve in alcohol. According to Tobler 100 parts of water dissolve:

At	10°	20°	29°	50°	70°
$CoSO_4$	30·5	36·4	40	55·2	65·7

When its solution is allowed to stand at from 40° to 50° monosymmetric crystals having the composition $CoSO_4+6H_2O$ are formed, and these are isomorphous with the corresponding zinc salt. If a concentrated solution of cobalt sulphate be poured gently into sulphuric acid a peach-blossom coloured powder $CoSO_4+4H_2O$ is deposited. All the hydrates lose their water on heating but do not fuse, becoming opaque and of a rose-red colour (Proust). Like nickel sulphate it forms numerous double salts.

Cobaltic Sulphate, $Co_2(SO_4)_3+18H_2O$, is deposited in blue, silky needles, when a cooled acid solution of cobaltous sulphate is electrolysed in a divided cell. It dissolves in water forming a blue solution which rapidly decomposes with evolution of

[1] Beylund, *Ber.* 1874, **7**, 469.

oxygen. The crystals decompose on exposure to the air, finally becoming pink. It forms a greenish-blue solution in dilute sulphuric acid, which gives a black precipitate with alkalis and is rapidly decomposed by reducing agents. Hydrochloric acid decomposes the salt with evolution of chlorine.[1]

Cobaltic Ammonium Alum, $(NH_4)_2SO_4+Co_2(SO_4)_3+24H_2O$, is obtained by adding ammonium sulphate to an acid solution of cobaltous sulphate and passing a weak current. It forms blue octahedra and is stable when dry, but decomposes in solution, ozonised oxygen being liberated. The potassium alum has similar properties (Marshall).

Cobalt and Nitrogen.

590 *Nitro-cobalt*, $Co_2(NO_2)$, is formed when diluted nitrogen peroxide is passed over reduced metallic cobalt. It is a black mass, which is vigorously decomposed by water, and explodes when mixed with combustible matter.[2]

Cobalt Nitrite. Neither cobaltous nor cobaltic nitrite has been prepared in the solid state. The double potassium salt described below differs in many of its properties from an ordinary nitrite, and is probably, like the cobalticyanides and the cobaltammine salts, a derivative of a complex acid containing cobalt.

Potassium Cobaltinitrite, $2K_3Co(NO_2)_6+3H_2O$, was discovered by Fischer,[3] and is obtained as a yellow precipitate when the solution of a cobaltous salt, acidified with acetic acid, is mixed with a solution of potassium nitrite:

$$CoCl_2+5KNO_2+2HNO_2=2K_3Co(NO_2)_6+2KCl+NO+H_2O.$$

As this salt is somewhat soluble in water, it is best to wash it with a solution of potassium acetate, and then with an 80 per cent. alcohol. Cobalt yellow, as this compound is also termed, is a bright yellow powder consisting of microscopic pyramids, or of four- or six-sided stellated forms. According to Sadtler[4] the salt is usually anhydrous; it can however be obtained, according to the concentration of the solution, with from one to four molecules of water, and its colour then varies

[1] Marshall, *Journ. Chem. Soc.* 1891, i. 760.
[2] Sabatier and Senderens, *Bull. Soc. Chim.* 1893 [3], **9**, 669.
[3] *Pogg. Ann.* 1848, **74**, 124. [4] *Amer. J. Sci.* [2], **49**, 189.

from a bright yellow to a dark greenish-yellow. It is decomposed by nitric and hydrochloric acids, but only when heated. Caustic potash solution attacks it with difficulty. Caustic soda or baryta water, on the other hand, decomposes it readily, on gently warming, with precipitation of the brown hydroxide. The salt suspended in water is only slowly attacked by sulphuretted hydrogen, but sulphide of ammonium instantly separates black sulphide of cobalt.

The cobalti-nitrites of ammonium, sodium, rubidium, and cæsium, are known; they are also yellow and crystalline. The compounds of the last two metals are distinguished by being only one-tenth as soluble as their chloroplatinates.[1]

$Rb_3Co(NO_2)_6+H_2O$ dissolves in 19,800 parts of water.
$Cs_3Co(NO_2)_6+H_2O$ „ 20,100 „

If a solution of cobalt chloride be precipitated with potassium nitrite without addition of acid, a yellow hydrated precipitate of potassium cobaltous nitrite, $2KNO_2+Co(NO_2)_2$, is obtained, soluble in hot water and yielding a red solution.[2]

Cobalt Nitrate, $Co(NO_3)_2+6H_2O$. This substance generally forms an indistinctly crystalline mass; it may be obtained by slow evaporation in monosymmetric prisms, having a specific gravity of 1·83 and not undergoing change in dry air. It begins to melt below 100°, and when more strongly heated the violet liquid becomes thick and green; then it begins to boil, giving off nitrous fumes, and the black oxide is left behind.

Ammoniacal Cobalt Compounds or Cobaltammine Salts.

591 In 1799 Tassaert[3] observed that a solution of a cobalt salt in ammonia assumes a brown colour on exposure to the air, and that this changes on boiling to a wine-red, whilst Thénard,[4] in 1802, stated that these changes were brought about by an absorption of oxygen. This latter observation was confirmed by Proust, who found that, on evaporating the solution, black cobaltic oxide separates out. The compounds which are thus formed have attracted the attention of many chemists,[5]

[1] Rosenbladt, *Ber.* 1886, **19**, 2531.
[2] Erdmann, *J. pr. Chem.* 1866, **97**, 385.
[3] *Ann. Chim.* 1799 (1), **28**, 95. [4] *Ann. Chim.* 1802, **42**, 210.
[5] Genth, *Annalen*, 1851, **80**, 275; Frémy, *Compt. Rend.* 1851, **32**, 509, 808; Claudet, *Phil. Mag.* 1851 [4], **2**, 253. A history of these compounds will be

but still the subject cannot be considered to have been exhausted.

These substances contain, for each atom of cobalt, from two to six molecules of ammonia and often other elements or groups of elements united to form a compound radical, which usually has a basic function and is capable of forming salts, acting like a mono-, di- or tri-valent metal, but sometimes has an acid function or is neutral. The salts thus produced are capable of undergoing numerous double decompositions giving rise to a very large number of derivatives, among which many cases of isomerism occur. Analogous compounds are formed by chromium, platinum, iridium and other metals of the platinum group, and it is probable that all these are closely allied in structure.

As already mentioned (p. 934) these compounds do not show the ordinary reaction of the metal but have characteristic reactions of their own, and the same is frequently true of many of the acid radicals which they contain, just as the chlorine in chloroform, for example, does not show the same reactions as that in sodium chloride, not being precipitated by silver nitrate. This is accounted for by supposing that in the above cases the acid radical forms part of the complex group containing the metal, whereas those acid radicals which give the ordinary reactions are outside the complex group. Thus only two-thirds of the total chlorine of the compound, $Co(NH_3)_5Cl_3$, is precipitated by silver nitrate, indicating that the formula of the compound is in reality $[Cl(NH_3)_5Co]Cl_2$. An additional proof that the above formula represents the constitution of the compounds is found in the fact that determinations of the electrical conductivity of its aqueous solution show that in dilute solution only three ions are formed,

$$[\overset{+}{Cl}(NH_3)_5\overset{+}{Co}],\ \overset{-}{Cl}+\overset{-}{Cl},$$

whereas if all the chlorine atoms had retained their usual function, at least four ions would have been produced (compare p. 85). The determination of the electrical conductivity of an aqueous solution of a salt is in fact the most reliable method of

found in *Untersuchungen der ammoniakalische Kobalt Verbindungen*, by Fr. Rose. Heidelberg: 1871. See also for the more recent work Jörgensen, *Zeit. anorg. Chem.* 1892, **2**, 279; 1894, **5**, 147; **7**, 289; 1896, **11**, 416; 1897, **13**, 172; **14**, 404; Werner, *Zeit. anorg. Chem.* 1893, **3**, 267; 1895, **8**, 153, 189; **9**, 382; 1897, **14**, 21, 28; Werner and Miolati, *Zeit. phys. Chem.* 1893, **12**, 35; 1894, **14**, 506.

ascertaining the composition of the various complex radicals in these compounds, but it has been found that in some cases the salt undergoes change when its aqueous solution is allowed to stand and the conductivity shows a corresponding variation.

The constitution of these complex radicals is still under discussion, two different views being held. According to one of these (Blomstrand, Jörgensen) the metal retains its characteristic valency in all the compounds, the molecules of ammonia being attached to the metal in open chains by virtue of the pentavalent character of nitrogen. That portion of the acid radicals which does not retain its ordinary properties is directly connected with the metal, whilst the other portion is combined with nitrogen. Water may take the place of one or more of the ammonia groups, the oxygen atom being supposed quadrivalent. The compound already referred to would thus receive such a constitutional formula as

$$Co \begin{cases} \diagup Cl \\ —NH_3.NH_3.Cl \\ \diagdown NH_3.NH_3.NH_3.NH_3.Cl. \end{cases}$$

The existence of isomerides can be readily expressed by a variation in the arrangement of the various groups.

According to the second view (Werner) the atom of cobalt has the power of combining directly not only with acid radicals but also with complete molecules such as those of ammonia and water, the total number of molecules and radicals thus combining to form the complex radical characteristic of the compound being always six. The combining power of the radical thus produced is found always to be equal to the difference between the normal valency of the metal and the number of acid radicals already included within the complex group containing the metal. Thus the group $[(NH_3)_6Co]$ containing no acid radicals is found to be trivalent, like cobalt itself in the cobaltic salts. The group $[Cl(NH_3)_5Co]$ containing *one* acid radical is divalent, whilst $[Cl_3(NH_3)_3Co]$ containing three acid radicals is a neutral compound. These six groups within the complex radical are supposed to be arranged symmetrically about the cobalt atom and thus may be said to occupy the six corners of an octahedron, at the centre of which the cobalt atom is situated, the external acid radicals being supposed to be further removed from the cobalt atom than the

others. The isomerism of the derivatives depends either on the position of the acid radical within or without the complex group or the relative arrangement of the various groups within the radical, and is, therefore, in many cases of a geometrical character.

These compounds are known as the *cobaltammines*, this spelling of the word being adopted to avoid confusion with the organic *amines*, which have an entirely different constitution. The nomenclature of these compounds has hitherto been founded on the colours characteristic of the various compounds, terms such as roseo, praseo, luteo, croceo, fuseo, xantho, &c., having been employed. A much more rational proposal has been made by Werner,[1] the principle of which is that the names of the various groups contained within the complex radical precede that of the metal, whereas those of the external groups follow it, this being nothing more than an adaptation of the nomenclature frequently employed for organic compounds.

Thus the compound $[Cl(NH_3)_5Co]Cl_2$, formerly known as purpureocobalt chloride, receives the name chloro-pentammine-cobaltic dichloride, whilst the compound $[H_2O.(NH_3)_5Co]Cl_3$ (roseocobaltic chloride) becomes aquo-pentammine-cobaltic trichloride, just as the organic compound $[C_6H_3Cl_2.CH_2]Cl$ is termed dichloro-benzyl chloride. Exactly the same considerations apply to the compounds of chromium, platinum, &c.

Only one or two typical compounds of each class of these derivatives are here described.

(1) *Hexammine salts* (*luteo-salts*), $[(NH_3)_6Co]R'_3$, are formed when dilute solutions of cobaltous salts, containing a large amount of ammonia and ammonium chloride, are exposed to the oxidising action of the air and are also produced by the action of ammonia on many of the salts containing five molecules of ammonia.

Hexammine-cobaltic chloride (*luteocobalt chloride*),

$$[(NH_3)_6Co]Cl_3,$$

is obtained when the ammoniacal cobalt chloride solution is allowed to stand for some time, especially in the presence of sal-ammoniac. The formation of the salt is facilitated by addition of oxidising substances such as lead dioxide, bromine, &c. (Braun, Mills). It crystallises in reddish-yellow monosymmetric prisms or pyramids, which dissolve slowly in cold but readily in hot water. It forms a difficultly soluble chloroplatinate.

[1] *Zeit. anorg. Chem.* 1897, **14**, 21.

(2) *Pentammine-cobalt salts* form two distinct classes of compounds.

(*a*) The *aquo-pentammine salts* (*roseo-salts*), in which one molecule of ammonia of the hexammine salts is replaced by water, the resulting group, $[H_2O(NH_3)_5Co]$, retaining its trivalent basic character.

(*b*) The members of the second class are characterised by the fact that the complex radical only contains five ammonia molecules together with a monovalent acid radical or its equivalent, the resulting group $[R'(NH_3)_5Co]$ being divalent. The compounds containing this radical have been distinguished by different names according to the nature of R, the salts of the various series usually possessing characteristic colours.

The aquopentammine salts, which are pink, lose water when heated with acids forming derivatives of the second class, whilst the latter are reconverted into aquopentammine salts by boiling or standing with water. As indicated by the formulæ, the salts of the second class contain one-third of their acid radical more firmly combined than the rest.

Chloro-pentammine-cobaltic chloride (*Chloropurpureo-cobaltic Chloride*), $[Cl(NH_3)_5Co]Cl_2$, is obtained by boiling a solution of roseo-cobaltic chloride; it falls as a red precipitate, soluble at 10° in 287 parts of water, and crystallising in quadratic prisms. With chloro-platinic acid it forms the salt, $[Cl(NH_3)_5Co]PtCl_6$, which is almost insoluble in cold water, and separates as a brownish-red powder. If the chloride be triturated with strong sulphuric acid a solution of *chloro-pentammine-cobaltic sulphate*, $[Cl(NH_3)_5Co]SO_4$, is formed, and if nitric acid be added to this solution fine red microscopical crystals of *chloro-pentammine-cobaltic nitrate*, $[Cl(NH_3)_5Co](NO_3)_2$, are thrown down, the solution of which is not precipitated by silver nitrate.

(3) *Tetrammine salts* are analogous to the pentammine salts, but the complex radical only contains four molecules of ammonia and two other groups, which may both be water or acid radicals, or may be one of each.

Dichloro-tetrammine-cobaltic chloride (*Praseo-cobaltic Chloride*), $[Cl_2(NH_3)_4Co]Cl + H_2O$, is usually formed together with the other cobaltammine chlorides. It crystallises in small glistening needles which possess an emerald green colour, whence the term praseo is derived. These dissolve in water yielding a green solution which soon becomes red, and undergoes decomposition on boiling. If fuseo-cobaltic chloride be warmed with

tolerably dilute hydrochloric acid a deep violet solution is obtained, and this on cooling deposits small violet octahedra which possess the same composition as the green salt, and pass into the latter when dissolved in concentrated sulphuric acid to which hydrochloric acid is gradually added.

Dinitrito-tetrammine-cobaltic Sulphate (*Croceo-cobaltic Sulphate*), $[(NO_2)_2(NH_3)_4Co]_2SO_4$, is formed when a mixture of solutions of cobalt sulphate and potassium nitrite saturated with ammonia is exposed to the air. It is deposited in orange-yellow crystals together with green cobaltic hydroxide. The mixture is filtered and the residue dissolved in hot dilute nitric acid, and from this solution the sulphate is obtained on cooling in the form of yellow quadratic tables. Large wine-red crystals are also obtained from dilute solutions. It is slightly soluble in boiling water.

(4) *Triammine compounds* are formed from the tetrammine salts by loss of ammonia. Although they contain three acid radicals they are neutral substances and do not form salts. In aqueous solution they act as non-electrolytes.

Trinitrito-triammine-cobalt, $[(NO_2)_3(NH_3)_3Co]$, is prepared by acting on cobaltous chloride solution with ammonia and potassium nitrite (Erdmann) and by the action of ammonium nitrite on cobaltous chloride in presence of acetic acid (Gibbs). The substances prepared by these methods are probably geometrical isomerides and are both practically non-electrolytes (Werner).

(5) *Diammine salts* have been very slightly investigated, but are of great interest because the complex radical contains four acid radicals, and unlike those already mentioned has an acid function.

Potassium Tetranitrito-diammine-cobaltate (Erdmann's salt), $[(NO_2)_4(NH_3)_2Co]K$, is obtained by adding ammonium chloride and potassium nitrite to a solution of cobaltous chloride and gently warming. It forms yellow rhombic crystals.

In addition to the classes of compounds already described a series of substances known as the oxycobaltiammines

$$[Co_2(NH_3)_{10}(OH)(O_2H)]R'_4.$$

has been investigated, the constitution of which is not understood. Many of the cobaltous salts, such as the chloride, sulphate, and nitrate, also unite with six molecules of ammonia, forming additive products which closely resemble the corresponding compounds of copper in their properties.

Cobalt and Phosphorus and Arsenic.

592 *Phosphides of Cobalt.*—When pieces of phosphorus are thrown on to ignited cobalt a metallic lustrous bluish-white brittle mass is formed. This tarnishes on exposure to air and melts at a lower temperature than cobalt and contains 6 per cent. of phosphorus. On heating it burns with formation of a dark-blue glass (Pelletier). When cobalt reduced in hydrogen is heated to dark redness in the vapour of phosphorus, a light-grey metallic lustrous mass is formed, containing 28·4 per cent. of phosphorus (Schrötter), and this corresponds nearly to the formula Co_4P_3. A compound Co_3P_2 is also formed as a black powder by igniting a normal phosphate in a current of hydrogen.

Cobalt Arsenide, $CoAs_3$, occurs as skutterrudite near Modum in Norway crystallised in octahedra or combinations as well as in the massive state. It possesses a colour from tin-white to a pale lead-grey, and usually contains small quantities of iron and sulphur.

Smaltite or tin-white cobalt, $CoAs_2$, usually contains varying quantities of iron and nickel, and occurs in tin-white octahedra or combinations as well as in the massive state in the Erzegebirge.

Cobaltite, cobalt-glance, or bright white cobalt, $CoAs_2+CoS_2$ or CoAsS, crystallises in the regular system usually in pyramid octahedra and their combinations, and a portion of the cobalt is usually replaced by iron. It has a silver-white colour inclining to red, and occurs at Tunneberg and other localities in Sweden, at Siegen in Westphalia, and the Bottolack Mine near St. Just in Cornwall. The most productive mines are those of Vena in Sweden, where it is found in mica-slate.

Phosphates and Arsenates of Cobalt.—The normal and monohydrogen cobalt salts of the different modifications of phosphoric acid are rose-red or violet-blue insoluble compounds. The di-hydrogen-orthophosphate is easily soluble in water and forms a gummy mass. The arsenates are similar bodies; the normal arsenate, $Co_3(AsO_4)_2+8H_2O$, occurs native as cobalt-bloom or erythine, in violet monosymmetric needles isomorphous with vivianite, or in earthy masses. *Zaffre* is also an impure basic arsenate obtained by roasting cobalt glance free from iron, or by dissolving the ore in nitric acid and precipitating with soda. This is also used for painting on porcelain.

Cobalt and Carbon.

593 *Carbonates of Cobalt.*—The normal salt, $CoCO_3$, is obtained as a bright-red powder, consisting of microscopic rhombohedra, by heating cobalt chloride to 140° with a solution of sodium bicarbonate saturated with carbon dioxide. The salt $CoCO_3 + 6H_2O$ is formed by allowing mixed solutions of cobalt nitrate and sodium bicarbonate saturated with carbon dioxide to stand exposed to a low temperature until the amorphous precipitate which is first formed becomes crystalline; the dry salt is converted into the anhydrous salt on warming. When a cold or hot solution of a cobalt salt is precipitated with normal or acid sodium carbonate, bluish or violet basic cobalt carbonates of varying composition are thrown down.

Cobaltous Cyanide, $Co(CN)_2 + 3H_2O$. This is a reddish precipitate obtained when solutions of potassium cyanide and a cobalt salt are brought together. It easily dissolves in excess of the precipitant forming the soluble double salt, $Co(CN)_2 + 2KCN$. If the solution be treated with dilute hydrochloric acid cobaltous cyanide is again precipitated, but if the solution be previously warmed this does not occur, inasmuch as potassium cobalticyanide is formed (see below).

The cobaltocyanides and cobalticyanides are analogous in composition to the ferro- and ferri-cyanides (p. 1021), and may be regarded as salts of a complex radical containing cobalt. The cobalt is not precipitated by the usual reagents, but the compounds, especially the cobalto-cyanides, are not so stable as the corresponding iron compounds.

Potassium Cobaltocyanide, $K_4[\overset{IV}{Co}(CN)_6]$, is a deep amethyst-coloured crystalline powder, which is obtained by dissolving cobaltous cyanide in potassium cyanide at a low temperature and precipitating with alcohol. On addition of an acid it at once yields the following salt.[1]

Potassium Cobalticyanide, $K_3[Co(CN)_6]'''$, is formed when an excess of potassium cyanide is added to a solution of a cobalt salt, together with a little acetic acid or hydrochloric acid and the liquid well boiled:

$$6KCN + 2Co(CN)_2 + 2HCN = 2K_3Co(CN)_6 + H_2.$$

Hydrogen is only evolved in the absence of air, whilst in the

[1] Descamps, *Ann. Chim. Phys.* 1881 (5), **24**, 193.

presence of air oxygen is absorbed and a corresponding amount of water produced.[1]

This salt crystallises in bright yellow crystals isomorphous with potassium ferricyanide.[2] Copper sulphate yields a blue and silver nitrate a white precipitate, the salts $Cu_3[Co(CN)_6]_2$ and $Ag_3Co(CN)_6$ being formed. Ferrous cobalticyanide, $Fe_3[Co(CN)_6]_2$ is a white precipitate, whilst cobaltous cobalticyanide, $Co_3[Co(CN)_6]_2''' + 14H_2O$, is a bright red precipitate which becomes anhydrous and blue when heated to 200°. When the copper salt is decomposed by sulphuretted hydrogen *cobalticyanic acid*, $H_3Co(CN)_6$, is formed, and this is deposited in colourless silky needles on evaporating the solution. It is deliquescent, has a strongly acid taste and reaction, and is not attacked even by strong nitric acid.

Cobalt and Silicon, Aluminium and Zinc.

594 *Silicates of Cobalt. Smalt.*—The silicates of cobalt do not occur as minerals in nature. Although certain specimens of ancient Egyptian glass have been found to be coloured blue by cobalt, the direct application of the ores of cobalt for this purpose appears to date from the 16th century. Smalt is a potash-glass intensely coloured blue by cobalt oxide. Up to the middle of this century smalt was largely used for colouring starch, paper, &c., but the introduction of artificial ultramarine has done much to diminish the demand for cobalt blue.

For the preparation of smalt, the ore such as speiss-cobalt or cobalt-glance, free as far as possible from iron and sulphur, is first carefully roasted so that the cobalt is mainly oxidised, whilst nickel, iron, copper, and bismuth remain for the most part unaltered and separate out when the mixture is melted with glass as an insoluble speiss. The roasted ore is then fused with a mixture of quartz-sand and potashes, the fusion being effected in large earthen pots, arranged in a furnace similar to that employed for the manufacture of plate-glass. The arsenides of nickel and iron sink to the bottom of the pot and the glass is ladled out into cold water. The blue glass is then ground with water to an impalpable powder under granite stones.

Smalt varies in composition according to the differences in

[1] See also Moore, *Chem. News*, 1893, **68**, 295.
[2] Gmelin, *Handbuch Org. Chem.* **1**, 397.

the ores, as also in the proportion of sand and potashes employed. Thus the amount of silica varies between 56 and 70 per cent., that of potash between 12 and 22, and that of cobalt between 6 and 16 per cent. In addition, smalt contains small quantities of alumina, ferric oxide, and frequently also lime and oxide of lead; the commoner varieties likewise contain oxide of nickel. Smalt has the advantage as a paint over ultramarine that its colour is not destroyed by the action of acids.

Together with smalt, two other pigments containing cobalt must be mentioned although their composition is undetermined.

Rinmann's Green is obtained either by precipitating a mixture of zinc sulphate and cobalt sulphate with soda and heating the washed precipitate, or by evaporating a solution of cobalt nitrate with oxide of zinc, or zinc nitrate, to dryness, and igniting the residue. A very intense green-coloured mass is obtained by heating zinc white with roseocobaltic chloride (see p. 1071) to a moderate red-heat.

Thénard's Blue or Cobalt Ultramarine. When alumina, or a salt of aluminium, is strongly heated with cobalt oxide or one of its salts, a fine blue-coloured compound is obtained. This is prepared on the large scale by heating a mixture of alumina with phosphate or arsenate of cobalt, and is used as a paint.

Detection and Estimation of Cobalt.

595 This metal is characterised by its black sulphide insoluble in acetic and dilute hydrochloric acids and by the fine blue colour which its compounds impart to the borax bead. If a cobalt compound be reduced on a carbonised match the metal is obtained in shining white magnetic particles, which dissolve in hydrochloric acid with a rose-red colour, the solution becoming blue on evaporation.

In the separation from other metals, already described under manganese (see p. 930), cobalt and nickel are always obtained together.

The best method for the qualitative detection of the two metals is based on Liebig's method for their estimation (see below). For this purpose the sulphides are dissolved in concentrated hydrochloric acid with the addition of a crystal of potassium chlorate, and the solution evaporated nearly to dryness and afterwards diluted with water. Potassium cyanide is

then added until the precipitated cyanides redissolve, a drop of acetic acid is added and the liquid boiled for a few minutes. The solution then contains potassium cobalticyanide and potassium nickel cyanide. The latter is at once decomposed by sodium hypochlorite in alkaline solution, whereas the former is not attacked by this reagent. The solution is therefore made alkaline with caustic soda and boiled with sodium hypochlorite. Nickel is precipitated as the black trihydroxide, which may be filtered off, washed and tested by the borax bead, whilst the cobalt can be detected in the filtrate by evaporating and testing the residue by one of the dry reactions.

Cobalt is much more readily precipitated in the form of sesquioxide than nickel; but although this fact is made use of in the commercial separation of the two, the method does not afford sufficiently accurate results for analytical purposes.

Cobalt chloride imparts to the non-luminous gas flame an evanescent rose-red colour, but this does not give any characteristic spectrum. The spark spectrum of the chloride contains a large number of bright lines, and the metal also gives a spectrum consisting of a large number of bright lines of which the following in the blue are the most characteristic (Thalén):

4868	4815	4780
4840	4793	

Cobalt is usually estimated as the oxide, Co_3O_4, which is obtained by strongly heating the monoxide, carbonate, nitrate, &c., in the air. It may also be weighed as metal obtained by the reduction of the nitrate or the chloride in hydrogen; and when it is combined with a volatile acid it may be determined as the anhydrous sulphate by heating the salt with sulphuric acid. The metal may also be estimated electrolytically.

Numerous methods, both gravimetric and volumetric, have been proposed for the quantitative separation and estimation of nickel and cobalt. Only the three most successful gravimetric processes are here described.[1]

Liebig's hydrocyanic acid method[2] has received many modifications, and may be applied to the quantitative separation of the metals in substantially the form which has been described above as a qualitative method. The solution containing

[1] A summary and critical examination of all these methods will be found in *Zeit. anal. Chem.* 1891, **30**, 227.

[2] *Annalen*, 1853, **87**, 128.

potassium cobalticyanide and potassium nickel cyanide may be treated with caustic soda and sodium hypochlorite as there described, or may be boiled with precipitated mercuric oxide, the whole of the nickel being precipitated as a mixture of oxides, which after ignition may be weighed as nickel monoxide. The filtrate is acidified with nitric acid, and mercurous nitrate added in excess. Mercurous cobalticyanide is precipitated and is converted by ignition into tricobalt tetroxide. Both in this and the succeeding methods one of the metals is frequently estimated indirectly. The two are precipitated together by caustic soda from a known volume of solution, and the mixed oxides weighed, the amount of one of the metals being then found by difference.

Another separation of nickel from cobalt depends upon the precipitation of potassium cobaltinitrite (see p. 1066). This is dried at 100° and weighed, and the nickel in the filtrate is precipitated by caustic potash, the precipitate boiled, well washed, and converted by ignition into the monoxide.

A very accurate method depends on the fact that nitroso-β-naphthol, $C_{10}H_6(OH)NO$, yields an insoluble compound with cobalt salts, but not with those of nickel.[1] The solution is therefore acidified with hydrochloric acid, and a solution of this reagent in acetic acid added. A very voluminous precipitate is formed, which is well washed and then ignited with a little oxalic acid, the cobalt being finally heated in hydrogen and weighed.

The atomic Weight of Cobalt, like that of nickel, has been frequently determined, but without any great degree of consistency. Rothhoff[2] converted a weighed quantity of the monoxide into the chloride and obtained the number 58·50. The relation between the carbon and cobalt in the oxalate gave Schneider[3] the number 59·58. Marignac,[4] by the analysis of the sulphate, obtained numbers varying from 58·20 to 58·32, whilst by the analysis of the anhydrous chloride he obtained similarly 58·28 to 58·40, and by that of the crystallised chloride 58·40 to 58·58. From numerous analyses of the cobaltammine salts Gibbs[5] deduced the number 58·56 as an average, whilst Dumas,[6] from the analysis of the chloride, obtained the number 58·56 to 58·73. Russell,[7] in fifteen closely agreeing experiments, obtained the

[1] Ilinski and Knorre, *Ber.* 1895, **18**, 699.
[2] *Pogg. Ann.* 1826, **8**, 185.
[3] *Pogg. Ann.* 1857, **101**, 387.
[4] *Arch. Phys. Nat.* (2), **1**, 373.
[5] *Amer. J. Sci.* [2], **25**, 483.
[6] *Ann. Chim. Phys.* 1859 [3], **55**, 129.
[7] *Journ. Chem. Soc.* 1863, 51.

number 58·3 by reducing the monoxide in a current of hydrogen. By dissolving the pure metal in hydrochloric acid and determining the amount of hydrogen evolved he likewise obtained the number 58·31 as a mean of four determinations.[1] Zimmermann,[2] also by reducing the oxide, has obtained 58·45.

Winkler has investigated the atomic weight of cobalt as well as that of nickel (p. 1056). His earlier determinations[3] gave the number 58·8, whilst the analysis of the chloride gave 59·37, and the action of iodine[4] on the pure metal 59·07. A later determination by Hempel and Thiele[5] has yielded them a lower result than that obtained by Winkler, the reduction of tricobalt tetroxide having given the number 58·56, and the analysis of the chloride 58·48. The atomic weight may, in the meantime, be taken as 59 (O = 15·88).

[1] *Chem. News*, 1869, **20**, 20.
[2] *Annalen*, 1885, **232**, 324.
[3] *Zeit. anal. Chem.* 1867, **6**, 22.
[4] *Zeit. anorg. Chem.* 1895, **8**, 1.
[5] *Zeit. anorg. Chem.* 1896, **11**, 73.

SUB-GROUP (*b*). THE RUTHENIUM GROUP.

596 The three metals of this group—ruthenium, rhodium, and palladium—all have a silvery lustre, and combine with oxygen at high temperatures rather more readily than the members of the platinum group, and also melt at a lower temperature. The salts of ruthenium and rhodium correspond to the sesquioxide, M_2O_3, whilst palladium forms two series of salts corresponding to the monoxide and dioxide, the former being the more stable. In addition, ruthenium yields salts of the acidic oxides RuO_3 and Ru_2O_7, and also, unlike the other two, yields a tetroxide, RuO_4.

All three metals give rise to series of ammoniacal bases, the properties and composition of which differ, however, in each case. The ruthenium bases all contain the nitroso-group, NO, in addition to ammonia; those of rhodium closely resemble the cobalt derivatives, and those of palladium correspond to two of the series yielded by platinum.

RUTHENIUM, Ru = 101·0.

597 In 1828 Osann[1] stated that he had discovered three new metals in the platinum ores from the Ural. To one of these he gave the name of *ruthenium*, from the name of Russia, the country in which it was found. In the following year, however, he withdrew the statement of the existence of one of the metals, and the existence of the other two remained doubtful until Claus, in 1845, examined the question. This chemist proved the existence of a new metal in the platinum ore, and retained for it the name of ruthenium because it was found to

[1] *Pogg. Ann.* 1828, **14**, 329; 1845, **64**, 197.

be contained in small quantity in the substance termed ruthenium oxide by Osann, which for the most part consisted of silica, zirconia, and the oxides of titanium and iron. Claus investigated the reactions of the metal and a large number of its derivatives.[1]

Ruthenium is found both in platinum ore and in osmiridium, whilst it occurs as sulphide in laurite, Ru_2S_3.[2]

Of the various methods of preparing the metal, that of Deville and Debray[3] is the most interesting, as these chemists prepared the metal on a large scale, and specially studied its physical properties. For this purpose, the alloy of osmiridium (p. 1115) containing ruthenium is fused with zinc, the regulus then treated with hydrochloric acid, and one part of the finely-divided residue mixed with three parts of barium dioxide and one part of barium nitrate, the mixture being heated for two hours to a temperature somewhat below the melting-point of silver. The cold mass is then reduced to an impalpable powder and thrown into dilute hydrochloric acid contained in a stoppered bottle. In this operation the liquid must be kept well cooled in order to prevent the escape of the vapours of poisonous osmium tetroxide, and the operation must be carried on in a good draught-place. As soon as the action is over, one part of nitric acid and two parts of sulphuric acid are added to the liquid, the mixture well shaken, the barium sulphate allowed to deposit, and the clear liquid poured off. The residue is washed by decantation and the liquid distilled until three-fourths of it have passed over. The distillate is worked up for osmium, whilst the concentrated residue, mixed with from two to three parts of sal-ammoniac and a small quantity of nitric acid, is dried on the water-bath. The residue is then washed with water which is half saturated with sal-ammoniac, until the filtrate is colourless. By this treatment ammonium chloriridate, containing some ruthenium, remains behind. This is ignited and the remaining spongy metallic mass fused for two hours in a silver basin with two parts of nitre and one part of caustic potash. The fused mass is then dissolved in water, and the characteristic orange-red solution of ruthenate of potassium treated with nitric acid until the yellow colour has disappeared,

[1] *Annalen*, 1845, **56**, 257; 1846, **59**, 234; *Pogg. Ann.* 1845, **64**, 622; **65**, 200; *Jahresb.* 1859, 257; 1860, 205; 1861, 320; 1863, 397.

[2] Wöhler, *Annalen*, 1864, **129**, 116.

[3] Deville and Debray, *Compt. Rend.* 1876, **83**, 926; 1879, **89**, 587.

when ruthenium oxide separates out, which, however, still contains silicic acid and some iridium and osmium; it is then ignited in a graphite crucible and fused in the oxyhydrogen furnace.

Another plan for preparing chemically pure ruthenium depends upon the facts that whilst osmium tetroxide is volatilised in a stream of air, the corresponding volatile tetroxide of ruthenium is only formed by the action of chlorine in alkaline ruthenium solution. Hence the metal, as obtained by other processes, must be heated in a current of oxygen until the whole of the osmium tetroxide has been volatilised and then fused a second time with potash and saltpetre, the mass dissolved in water, saturated with chlorine, and distilled in a stream of chlorine on the water-bath, when pure ruthenium tetroxide volatilises. This is then dissolved in caustic potash and the ruthenium oxide precipitated from the solution by alcohol, and this again reduced to metal by ignition in a stream of coal-gas or hydrogen.

In order to obtain the metal in the crystalline state it may be fused in a carbon crucible with from five to six times its weight of tin, the alloy being treated with boiling hydrochloric acid which leaves the compound $RuSn_3$ undissolved; this when ignited in a carbon-boat in a current of hydrochloric acid gas leaves a residue of crystallised ruthenium.

Fused ruthenium has a specific gravity of 12·063 at 0°; like iridium it is hard and brittle, and next to osmium is the most infusible metal of the group. With the exception of the latter metal, it is also the one which combines most readily with oxygen, the fused metal becoming covered with a brown film in the air, and on cooling it spirts like silver and iridium. When heated in a current of oxygen it yields the dioxide, and at temperatures of about 1000° some tetroxide is also formed, although this substance decomposes when heated by itself at 107°.[1] The pure metal is scarcely attacked even by aqua-regia, but it combines with chlorine at a red heat.

[1] Debray and Joly, *Compt. Rend.* 1888, **106**, 100.

RUTHENIUM COMPOUNDS.

Ruthenium and Oxygen.

598 The following oxides of ruthenium have been described: RuO, Ru_2O_3 (?), RuO_2, and RuO_4, and in addition salts corresponding to the acidic oxides RuO_3 and Ru_2O_7 have been prepared.

Ruthenium Monoxide, RuO.—If the finely-divided metal be frequently powdered, and after each pulverisation ignited in chlorine, the dichloride of ruthenium is obtained as a black, partially crystalline mass, insoluble in acids. By calcining the dichloride mixed with sodium carbonate in a current of carbon dioxide and washing the residue with water, ruthenium monoxide remains as a dark grey powder, which is not attacked by acids.

Ruthenium Sesquioxide, Ru_2O_3, is obtained according to Claus as an indigo-blue powder insoluble in acids by heating the finely-divided metal to redness for some time in contact with air. Debray and Joly were however unable to obtain it. The *trihydroxide*, $Ru(OH)_3$, is obtained by precipitating the corresponding chloride with an alkali. It forms a blackish-brown precipitate, which even after long washing retains from three to four per cent. of alkali. It dissolves with a yellow colour in acids, but is insoluble in water and alkalis.

The ruthenious salts are derived from the sesquioxide, and of these only a few of the haloid compounds are known. The chloride and its double salts dissolve in water with a reddish-yellow colour. This solution deposits on standing, slowly in the cold but quickly when warmed, a black very finely-divided precipitate of oxychloride. This reaction is so delicate that one part of the metal imparts a distinct ink-like colour to 100,000 parts of water.

Ruthenium Dioxide, RuO_2.—This is obtained by roasting the disulphide or sulphate in contact with air. It is likewise formed when the metal is fused in an oxidising atmosphere, when it burns with a sparkling smoky flame, and evolves an ozone-like smell. Hence this compound can be easily obtained from the ruthenium contained in the osmiridium alloy, which may for this purpose be heated in a porcelain tube to the

melting-point of copper, in a current of pure air, from which all organic substance has previously been carefully separated. The ruthenium dioxide is carried forward by the osmium tetroxide formed at the same time, and deposited in the cold part of the tube, whilst the more volatile osmium compound is carried on still further by the current of air. Ruthenium dioxide crystallises in small very hard quadratic pyramids, possessing a green metallic lustre, and a bluish or greenish iridescence. These have a specific gravity of 7·2, and are isomorphous with cassiterite and rutile (Rammelsberg).

Ruthenium Tetrahydroxide, $Ru(OH)_4+3H_2O$, is obtained by evaporating ruthenium disulphate with caustic potash, when a dark red precipitate falls down. This contains some alkali, and dries to a reddish-brown mass, giving off water at 300°. When more strongly heated it deflagrates with vivid incandescence and evolution of a black soot-like smoke. It is soluble in acids and alkalis, yielding yellow solutions.

Neither the oxides RuO_3 and Ru_2O_7 nor the corresponding acids have been prepared, but salts are known corresponding to these.

Potassium Ruthenate, $K_2RuO_4+H_2O$, is obtained by igniting a mixture of ruthenium, caustic potash and potassium nitrate or carbonate, or by the action of 50 grams of the tetroxide on a solution of 70 grams of caustic potash in 500 c.c. of water at 60°; it crystallises from water in rhombic crystals having the above composition, which have a green metallic reflex, and are red in transmitted light. They take up moisture and carbon dioxide from the air and lose all their water at 200°. *Potassium perruthenate*, $KRuO_4+H_2O$, is prepared by the action of chlorine on a solution of the foregoing salt or by dissolving 60 grams of caustic potash in 250 c.c. of water, warming to 60° and adding 50 grams of ruthenium tetroxide previously fused under water. It forms black lustrous quadratic octahedra. When heated in a vacuum at 400° it decomposes with formation of oxygen, ruthenium dioxide and the ruthenate, or possibly a salt of potassium with a lower oxide.[1]

Ruthenium Tetroxide, RuO_4.—This compound, as already stated, is formed in small quantity when the metal is heated at 1000° in a current of oxygen, although when heated alone it decomposes at 106–107°. It is prepared by passing chlorine into a solution of potassium nitrosochlororuthenate or of potas-

[1] Debray and Joly, *Compt. Rend.* 1888, **106**, 1494; 1891, **113**, 694.

sium ruthenate; the liquid becomes heated and the tetroxide distils over, and is deposited in the receiver. It is best purified by distillation through anhydrous calcium chloride in a vacuum, the apparatus employed being carefully freed from organic matter. It melts at 25·5°, the liquid readily remaining superfused, and solidifying to a vitreous mass. When heated it does not boil at 106° and decomposes at 106–107° with a smoky flame but no explosion, the crystalline dioxide being formed. It may, however, be volatilised under reduced pressure, having a vapour tension of 20 mm. at 42° and of 183 mm. at 100·8°.

The moist oxide quickly decomposes; in the dry state it is fairly stable, but decomposes in sunlight with formation of lower oxides. It dissolves slowly in water, and the solution when it contains free chlorine or hypochlorous acid may be kept without alteration for some days if light be excluded. The vapour has a yellow colour and an irritating odour resembling that of ozone or nitrous fumes, and attacks the mucous membrane; it blackens organic matter rapidly, and is immediately reduced by alcoholic potash with separation of finely-divided metallic ruthenium.[1]

Ruthenium and the Halogens, Sulphur and Nitrogen.

599 *Ruthenium Dichloride*, $RuCl_2$, is obtained as a black crystalline powder by the long-continued action of chlorine on powdered ruthenium at a dull red heat; it is insoluble in acids and aqua-regia, and is only slightly attacked by caustic potash.

Ruthenium Trichloride, $RuCl_3$, is formed when the finely-divided metal is heated in a mixture of chlorine and carbonic oxide at 360–440°, and is a dark brown substance which is insoluble in water but dissolves in absolute alcohol, forming a purple-violet solution; on exposure to moisture the colour gradually changes to a deep indigo blue, owing to the formation of a hydroxychloride.

A ruthenium trichloride and tetrachloride and double salts of these with alkali chlorides have been described by Claus, but later investigation [2] has shown that these all contain nitrogen, and are in reality nitroso-derivatives (p. 1086).

[1] Debray and Joly, *Compt. Rend.* 1888, **106**, 328; Joly, *Compt. Rend.* 1891, **113**, 693.

[2] Joly, *Compt. Rend.* 1888, **107**, 994; Howe, *Amer. Chem. J.* 1894, **16**, 388.

Ruthenium Sulphide, Ru_2S_3.—This compound occurs as the mineral laurite which is found with platinum ore in Borneo and Oregon, and usually contains a small percentage of osmium. It crystallises in small octahedra, usually showing also cube faces. Sulphuretted hydrogen gives a precipitate with solutions of ruthenium salts, which consists of a varying mixture of sulphides and oxysulphides of ruthenium with free sulphur.

Ruthenic Sulphate, $Ru(SO_4)_2$, is obtained by dissolving the precipitated sulphides in nitric acid; the reddish-yellow solution leaves on evaporation a yellowish-brown amorphous mass which yields a deliquescent powder closely resembling mosaic gold.

Ruthenium and Nitrogen. When brown ruthenium trioxide is dissolved in nitric acid it forms a red nitrate; the latter on boiling with successive quantities of hydrochloric acid and evaporation at 120° yields a red crystalline mass of ruthenium nitrosochloride, $RuCl_3NO + H_2O$; on recrystallisation from hot water this forms dichroic asymmetric prisms having the composition $RuCl_3.NO + 5H_2O$, which rapidly effloresce in dry air. This substance combines with alkali chlorides forming double salts, which are identical with the substances formerly supposed to be double salts of ruthenium trichloride and the alkali chlorides.[1] The potassium salt has the composition $RuCl_3.NO,2KCl$, and forms a violet-brown iridescent powder consisting of orange-red microscopic cubes.

Ammoniacal Derivatives of Ruthenium.

600 Like most of the other members of this group, ruthenium forms a number of derivatives, the basic radical of which contains both ruthenium and ammonia. These were first examined by Claus, who described a series of salts derived from the hydroxides $Ru(NH_3)_4(OH)_2$, and also obtained a hydroxide to which he assigned the composition $Ru(NH_3)_2(OH)_2$. According to Joly,[2] however, the salts containing four molecules of ammonia also contain the nitroso-group, and have the general formula $Ru(NH_3)_4NO.OH.X_2$, where X is a halogen or monovalent acid radical, whilst the hydroxide containing two molecules of ammonia has the composition $Ru(NH_3)_2NO(OH)_3 + H_2O$.

[1] Joly, *Compt. Rend.* 1888, **107**, 994; 1889, **108**, 1300.

[2] *Compt. Rend.* 1889, **108**, 1300; 1890, **111**, 969; 1893, **115**, 1299; Howe, *J. Amer. Chem. Soc.* 1894, **16**, 388.

The salts of the first-named series are well crystallised substances which usually have a golden-yellow colour, but no crystalline salts have been prepared from the second hydroxide.

Ruthenium and Carbon.

Ruthenocyanides. These compounds correspond to the ferrocyanides; the *potassium* salt, $K_4Ru(CN)_6+3H_2O$, is obtained by heating potassium nitrosochlororuthenate with potassium cyanide, and forms colourless crystals isomorphous with those of potassium ferrocyanide. Its solution is turned a bright violet colour by ferrous salts and a dark violet by ferric salts, whilst the salts of mercury, lead, and zinc yield white precipitates. The free *ruthenocyanic acid*, $H_4Ru(CN)_6$, is prepared from the potassium salt by adding hydrochloric acid and extracting with ether, and crystallises in pearly laminæ, readily soluble in water and alcohol. The solution has an acid reaction and an astringent taste, and on exposure to air assumes a blue colour (Claus).

Detection and Estimation of Ruthenium.

601 The ruthenic salts give a dark red precipitate with concentrated solutions of potassium chloride and ammonium chloride, and on boiling with water the characteristic ruthenium oxychloride is formed. Ruthenium solutions are first coloured blue by sulphuretted hydrogen, and afterwards the brown sulphide is formed, which is almost insoluble in ammonium sulphide. The production of the volatile tetroxide is also a characteristic reaction.

Ruthenium, like the other members of this group, is estimated quantitatively as the metal.

Atomic Weight of Ruthenium.—Claus[1] obtained the number 103·0, but the later investigations of Joly[2] with carefully purified material have shown that this figure is too high. The latter chemist determined the atomic weight (1) by reducing the dioxide in hydrogen; (2) by the reduction of the nitrosochloride in hydrogen; and (3) by the reduction of ammonium nitrosochlororuthenate, the numbers obtained being respectively 100·91, 100·99, and 100·89, and the atomic weight may therefore be taken as 101 (O = 15·88).

[1] *Petersb. Akad. Bull.* **3**, 353. [2] Joly, *Compt. Rend.* 1889, **108**, 946.

RHODIUM. Rh = 102·2.

602 When Wollaston[1] in 1804 first acknowledged that he was the discoverer of palladium (p. 1094), he likewise intimated that he had found another new metal in platinum ore, to which he gave the name of rhodium, because the solutions of this salt possess a rose-red colour (*ῥόδον*, a rose). After Wollaston's time the metal and its compounds were investigated by Berzelius and Claus. In addition to its occurrence in platinum ore, rhodium has been found, according to Del Rio, alloyed with gold as rhodium-gold.

In order to prepare rhodium from the mixed platinum metals, the solution is employed from which ammonium chloroplatinate has been precipitated. The metals still in solution are then precipitated by metallic iron, and, according to the process of Deville and Debray, the metallic precipitate is fused with one part of lead and two parts of litharge. A regulus is thus obtained, from which the lead, copper, and palladium may be dissolved out by the action of dilute nitric acid. The insoluble metallic powder is then well mixed with five parts of barium dioxide and heated to redness for two hours, the solid mass being lixiviated with water, and the residue boiled with aqua-regia in order to volatilise the osmium tetroxide, this latter being condensed. The excess of barium is precipitated from the solution by sulphuric acid, the filtrate evaporated at 100° with an excess of sal-ammoniac, and the residue washed with sal-ammoniac solution as long as the wash-water has a rose-red colour. The filtrate is then evaporated with an excess of nitric acid in order to decompose the sal-ammoniac, and the residual mass heated to redness with from three to four parts of sulphur. It is then rapidly boiled out with aqua-regia and sulphuric acid, and by this treatment nearly pure rhodium remains behind. In order further to purify this, it is fused with from three to four parts of zinc, and the alloy treated with strong hydrochloric acid, when the compound $RhZn_2$ remains behind. This is dissolved in aqua-regia and evaporated with an excess of ammonia. Rhodammonium chloride, $Rh(NH_3)_5Cl$, separates out, and this is then purified by recrystallisation, and ignited in a carbon crucible with some sulphur, and, lastly, in

[1] *Phil. Trans.* 1804, 419.

order to remove from it the last traces of silicon and osmium, fused in the oxyhydrogen furnace.

Another method of preparing the pure metal is that described by Bunsen,[1] for the particulars of which his memoir on the subject must be consulted. He obtained from one kilogram of the platinum residues from the St. Petersburg mint 33·2 grams of pure rhodium sodium sulphate, $Na_3Rh(SO_4)_3$.

Properties.—Rhodium possesses the colour and lustre of aluminium and has a specific gravity of 12·1. It fuses with greater difficulty than platinum, and spits on cooling, the surface becoming coloured blue from oxidation. When a solution of one of its salts is heated with sodium formate, the metal is precipitated in the form of a fine black powder, possessing the property of decomposing formic acid, CH_2O_2, with evolution of heat, into hydrogen and carbon dioxide. After a time the action becomes weaker, but the powder then simply requires to be washed with water and dried in the air to enable it to regain its original activity. At a somewhat higher temperature, and in presence of caustic potash, it also decomposes alcohol, C_2H_6O, with evolution of hydrogen and formation of potassium acetate, $C_2H_3O_2K$, and does not lose this power at a temperature at which glass begins to soften (Deville and Debray). Pure rhodium, as well as that which contains gold and platinum, is almost insoluble in acids. If, however, it be alloyed with bismuth, zinc, lead, or copper, it dissolves in aqua-regia. Alloys of much platinum and little rhodium dissolve also in aqua-regia, but if the rhodium be present in larger quantity much remains undissolved. Rhodium can, however, be brought into solution by repeated ignition with fused potassium hydrogen sulphate, as well as with phosphoric acid or acid phosphates. Of all the platinum metals rhodium is the most easily attacked by chlorine. Rhodium combines with tin, yielding the alloy $RhSn_3$, which forms small brilliant crystals.[2]

[1] *Phil. Mag.* 1868 [4], **36**, 253.
[2] Debray, *Compt. Rend.* 1887, **104**, 1470.

RHODIUM COMPOUNDS.

Rhodium and Oxygen.

603 Rhodium forms three oxides, having the formulæ RhO, Rh_2O_3, and RhO_2.

Rhodium Monoxide, RhO, is obtained by heating the trihydroxide, $Rh(OH)_3$, by the cupellation of an alloy of rhodium and lead, or by igniting the finely-divided metal in a current of air. It is a grey powder with metallic appearance, which is not attacked by acids, and when heated in hydrogen is reduced with evolution of light.

Rhodium Sesquioxide, Rh_2O_3, is obtained as a grey iridescent spongy mass by heating the nitrate. It is also formed as a crystalline mass when sodium chlororhodate is heated in oxygen. It is perfectly insoluble in acids.

Rhodium Trihydroxide, $Rh(OH)_3$, is a black gelatinous precipitate, obtained by heating a solution of sodium chlororhodate with excess of caustic potash. On drying it forms a heavy dark brown metallic lustrous mass having a conchoidal fracture. It is scarcely attacked by acids, hydrochloric acid dissolving it but very slightly.

If a solution of the sodium double salt be treated in the cold with potash not in excess, it becomes opaque, and on long standing deposits thin lemon-yellow crystals of the hydrate $Rh(OH)_3+H_2O$, which dissolve readily in acids, and, when moist, in caustic potash.

The rhodium salts are derived from the sesquioxide. They possess either a dark red or a yellow colour, and have a bitter but not astringent taste.

Rhodium Dioxide, RhO_2, is obtained by repeated fusion of the metal with caustic potash and saltpetre. The sesquioxide is first formed, and this undergoes further oxidation. It closely resembles the sesquioxide; it is attacked neither by alkalis nor by acids, and is reduced by hydrogen only at a high temperature.

Rhodium Tetrahydroxide, $Rh(OH)_4$.—When chlorine is passed into the alkaline solution of the sesquihydroxide for a long time and caustic potash occasionally added, this compound separates out as a green powder, the liquid becoming of a

blue or violet tint. The green powder dissolves in hydrochloric acid, yielding a blue solution, and this colour gradually changes to dark red, chlorine being evolved. The violet-blue solution probably contains the potassium salt of a rhodic acid, which latter separates out after some time as a blue powder, gas being simultaneously evolved. On drying, it is converted into the tetrahydroxide.

Rhodium Salts.

604 *Rhodium Trichloride*, $RhCl_3$, is obtained by the continued ignition of the finely-divided metal in chlorine, and also by heating one of the alkali double salts with sulphuric acid, and pouring the cooled mixture into water; a rose-red powder of insoluble rhodium chloride remains behind. It is also obtained as a brick-red powder by heating the rhodium tin alloy $RhSn_3$ in chlorine at 440°, the tin volatilising as stannic chloride. When the yellow hydroxide is dissolved in hydrochloric acid, a yellow solution is obtained possessing an astringent taste, which on concentration becomes rose-red, and then possesses the peculiar bitter taste characteristic of all rhodium salts. When this solution is evaporated, a dark red amorphous mass of the hydrated chloride is obtained which is deliquescent, and on further heating yields the insoluble anhydrous chloride.

The trichloride yields a large number of well-crystallised *chlororhodates*. The *sodium* salt, $3NaCl,RhCl_3+9H_2O$, crystallises in deep cherry-red asymmetric prisms, which are very soluble in water, and effloresce in the air to a peach-blossom coloured powder.

The *potassium* salt, $2KCl,RhCl_3$, crystallises in dark red acicular prisms which contain one molecule of water according to Berzelius, but according to Leidié are anhydrous. A hydrated chloride of the composition $3KCl_3,RhCl_3+3H_2O$ has also been described by Claus, which crystallises in dark-red asymmetric prisms. The *ammonium* salt, $2(3NH_4Cl,RhCl_3)+3H_2O$, forms four-sided rhombic prisms.

Rhodium Monosulphide, RhS.—When rhodium is heated in sulphur vapour it takes fire with formation of the sulphide, which is also produced when sulphuretted hydrogen is passed through a solution of a rhodium salt, and the washed precipitate dried by ignition in a current of carbon dioxide. Thus

obtained, it forms a bluish-white fused mass having a metallic lustre, which, when heated in the air, leaves a residue of spongy rhodium.

Rhodium Sesquisulphide, Rh_2S_3, is obtained in the pure state by heating the trichloride in sulphuretted hydrogen at 360°, and forms blackish crystalline plates. The *hydrosulphide*, $Rh(SH)_3$, is precipitated when sulphuretted hydrogen in large excess is passed into a solution of a rhodium salt at 100°, and forms a brownish-black precipitate which is insoluble in ammonium sulphide.[1]

Rhodium Sulphite, $Rh_2(SO_3)_3+6H_2O$, is obtained by dissolving the yellow hydroxide in sulphurous acid and evaporating. It is a pale yellow indistinctly crystalline mass, and forms crystalline double salts.

Rhodium Sulphate, $Rh_2(SO_3)_3+12H_2O$, is obtained by dissolving the yellow hydroxide in sulphuric acid, evaporating, and washing away the excess of acid by alcohol. It is a yellow crystalline mass which possesses a sour astringent taste. The anhydrous salt is a brick-red non-hygroscopic powder (Leidié). According to Claus it forms crystalline double salts with the alkali sulphates, but Leidié was unable to confirm this statement.

Rhodium Nitrite, $Rh(NO_2)_2$, has not been isolated, but forms characteristic double salts. *Sodium rhodionitrite*,

$$3NaNO_2,Rh(NO_2)_2,$$

separates in bulky white crystals, which act on polarised light. The *potassium* salt also forms white microscopic crystals when pure,[2] but is usually obtained as a heavy orange-coloured crystalline powder, which dissolves readily in hydrochloric acid.

Rhodium Nitrate, $Rh(NO_3)_3$, does not crystallise but forms a dark yellow hygroscopic gummy mass.

Potassium Rhodicyanide, $K_3Rh(CN)_6$, is obtained in a similar way to the corresponding iridium salt (see p. 1122), which it closely resembles, but may be distinguished from it inasmuch as acetic acid produces a pale crimson-red precipitate of rhodium cyanide, $Rh(CN)_3$, which dissolves in the cyanides of the alkali-metals, forming the rhodicyanides (Martius).

[1] Leidié, *Compt. Rend.* 1888, **106**, 1533.
[2] Leidié, *Compt. Rend.* 1890, **111**, 106.

Ammoniacal Derivatives of Rhodium.

605 The ammoniacal rhodium bases and salts closely resemble the corresponding cobalt compounds. The three chief series have the following general formulæ:

Hexammine Salts (Luteo-salts) $[(NH_3)_6Rh]R'_3$
Aquopentammine Salts (Roseo-salts) $[H_2O(NH_3)_5Rh]R'_3$
Pentammine Salts (Purpureo-salts) $[R'(NH_3)_5Rh]R'_2$

in which R′ is a monovalent negative radical.

Hexammine-Rhodium Trichloride (*Luteorhodium chloride*), $[(NH_3)_6Rh]Cl_3$, is obtained in colourless lustrous crystals by heating the salt next described with ammonia.

Chloropentammine-Rhodium Dichloride (*Chloropurpureorhodium chloride*), $[Cl(NH_3)_5Rh]Cl_2$, is prepared by dissolving the alloy of rhodium and zinc in aqua-regia and adding ammonia. It forms small yellowish lustrous rhombic crystals.

Aquopentammine-Rhodium Chloride (*Roseorhodium chloride*), $[H_2O(NH_3)_5Rh]Cl_3+H_2O$, is obtained by digesting the foregoing compound with silver oxide for several days, and dissolving the resulting base in hydrochloric acid.

Detection and Estimation of Rhodium.

606 Solutions of this metal are precipitated by sulphuretted hydrogen slowly in the cold, but more quickly when warmed. The brown sulphide is insoluble in ammonium sulphide. When a rhodium compound is heated in hydrogen the metal is obtained; this is insoluble in aqua-regia, but can be obtained in solution when it is fused with acid potassium sulphate; the fused mass on treatment with water yields a red solution. From this the metal is precipitated as a black powder on addition of caustic potash and alcohol. It is also precipitated from acid solution by zinc and other metals.

Rhodium is determined quantitatively as the metal.

Atomic Weight of Rhodium.—The earlier determinations of the atomic weight by Berzelius and Claus gave the number 103·2, but later determinations have shown that this number is too high. Jörgensen,[1] from the analysis of chloropentammine-

[1] *J. pr. Chem.* 1883 [2], **27**, 486.

rhodium dichloride and of the analogous dibromide, obtained the number 102·3, and Seubert and Kobbe,[1] by the same method, the number 102·2.

PALLADIUM, Pd = 105.

607 In April, 1803, a printed notice[2] came into the hands of Chenevix, to the effect that a new metal, called Palladium, was to be sold at Forster's, of Gerrard Street, Soho. Chenevix,[3] believing that this was simply a fraud, bought the whole stock and after investigating the question he came to the conclusion that the substance was not a new metal, but that it was a platinum amalgam of peculiar properties. Soon after the communication of Chenevix's paper to the Royal Society (May 13, 1803), an advertisement appeared in which a handsome reward was offered to any one who should prepare even a grain of this substance, either according to Chenevix's plan, or by any other method. No one succeeded in obtaining the reward, although several German chemists endeavoured to prepare the new substance. In 1804 Wollaston[4] declared that he was the discoverer of palladium, having taken this name from that of a new planet Pallas, discovered by Olbers in 1802. At the same time he described the process which he adopted in order to obtain the new metal from platinum ore.

Palladium occurs in a tolerably pure state with Brazilian platinum ore, as well as together with gold, at Tilkerode, in the Harz. It is also contained in most platinum ores, and is found in many places in South America alloyed with gold.

Numerous methods of separating palladium from the other

[1] *Annalen*, 1891, **260**, 314.

[2] "Palladium, or new silver, has these properties amongst others that show it to be a new noble metal:—1. It dissolves in pure spirit of nitre, and makes a dark-red solution. 2. Green vitriol throws it down in the state of a regulus from this solution, as it always does gold from aqua-regia. 3. If you evaporate the solution you get a red calx that dissolves in spirit of salt or other acids. 4. It is thrown down by quicksilver, and by all the metals but gold, platinum, and silver. 5. Its specific gravity by hammering was only 11·3; but by flattening as much as 11·8. 6. In a common fire the face of it tarnishes a little and turns blue, but comes bright again, like other noble metals, on being stronger heated. 7. The greatest heat of a blacksmith's fire would hardly melt it; 8. But, if you touch it while hot with a small bit of sulphur, it runs as easily as zinc."

[3] *Phil. Trans.* 1803, 290.

[4] *Phil. Trans.* 1804, 428; 1805, 316.

platinum metals have been described. Among these may be mentioned the precipitation of the dicyanide by the addition of mercuric cyanide to a neutral solution of a palladium salt, and the treatment of the dichloride solution with potassium iodide, which yields palladious iodide as a black insoluble precipitate. The cyanide is converted into the metal by ignition, and the iodide by heating in a current of hydrogen. Bunsen[1] by the iodide method prepared pure palladium from the platinum residues of the St. Petersburg mint, which consist of a mixture of all the platinum metals. Other methods of working up the platinum metals on the large scale have been given by Philipp[2] and Guyard.[3] From the palladium gold alloy it may be obtained by fusing the latter with silver, and treating the granulated metal with moderately dilute nitric acid, which dissolves the silver and palladium, but leaves the gold unattacked. The silver is precipitated with sodium chloride, and the palladium from the filtrate by metallic zinc.[4]

To prepare pure palladium from the commercial metal, it is dissolved in aqua-regia, and precipitated as the double ammonium chloride together with platinum and other metals. The precipitate is treated with excess of ammonia, when the palladium salt dissolves, and on treatment with hydrochloric acid yields, after a time, a precipitate of yellow palladdiammonium chloride. This sometimes contains rhodammonium chloride, which is separated by retreatment with ammonia and again treating with hydrochloric acid. The washed precipitate yields spongy palladium on ignition.

Palladium has a colour closely resembling that of silver and platinum, a specific gravity of 11·4 at 22·5° (Deville and Debray), and of all the platinum metals has the lowest melting-point, which is stated as 1360—1380° by Becquerel and as 1500° by Violle. At the melting-point of iridium it boils violently, undergoing partial oxidation and emitting green vapours, which condense to a brown sublimate consisting of a mixture of oxide and metal.

Palladium is dimorphous. The native metal occurs in the Brazils in the form of sand or rounded grains, amongst which small regular octahedra are sometimes found. Native palladium usually contains small quantities of both platinum and iridium, and has a specific gravity varying from 11·3 to 11·8. The

[1] *Phil. Mag.* 1868 [4], **36**, 253. [2] *Dingl. Polyt. Journ.* 1876, **220**, 95.
[3] *Compt. Rend.* 1863, **56**, 1177. [4] Cox, *Phil. Mag.* **23**, 16.

palladium found in the Harz occurs in small hexagonal tables, together with gold and lead selenide, and hence this latter body was first considered to be palladium selenide. Owing to the difference of crystalline form this variety has been termed by Dana[1] *Allopalladium.*

When palladium is heated to dark redness it assumes a violet or blue colour, but at higher temperatures it regains its metallic lustre, and this remains even when the metal is quickly cooled by plunging into water. At 450° it yields the oxide Pd_2O,[2] and when heated in a current of oxygen till the weight is constant forms the monoxide PdO.[3] Palladium dissolves readily in hot nitric acid, especially when this contains nitrous acid, or when the metal is alloyed with either copper or silver. Spongy palladium also dissolves in hydrochloric acid in contact with the air, and the compact metal likewise dissolves in this acid if chlorine be passed into the liquid, and is attacked by boiling concentrated sulphuric acid, and by fused potassium bisulphate. When warm palladium foil is brought into an electrolytic mixture of hydrogen or oxygen, or other explosive gaseous mixture, combination takes place without explosion (Coquillon),[4] and when the metal is brought into the flame of alcohol or coal-gas it becomes covered with a thick film of soot. When palladium sponge is placed in a current of ethylene this gas is decomposed with separation of carbon, and this occurs at a temperature at which the gas alone does not undergo any alteration.[5]

Palladium has not been employed very largely in the arts. For certain special purposes, however, it is useful; thus on account of its unalterability in the air, and owing to its bright silver-white colour, it has been employed for the preparation of graduated surfaces for astronomical instruments. It is likewise used for coating silver goods, as palladium does not lose its fine white colour on exposure to sulphuretted hydrogen, and hence it has also been much employed by dentists as a substitute for gold.

[1] *Mineralogy*, 5 ed. p. 12.
[2] Neumann, *Monatsh.* 1892, **13**, 40.
[3] Wilm, *Ber.* 1892, **25**. 220.
[4] *Compt. Rend.* 1876, **83**, 709.
[5] Wöhler, *Annalen*, 1876, **184**, 128.

PALLADIUM COMPOUNDS.

Palladium and Oxygen.

608 *Palladium Suboxide*, Pd_2O, is obtained by heating the metal in oxygen at 450°, or by the moderate ignition of basic palladium carbonate. It is a black powder, which is readily further oxidised, and is reduced by hydrogen at a red heat, steam being evolved with almost explosive violence. Acids decompose it into the metal and a palladious salt.

Palladium Monoxide, PdO, is formed by the long-continued heating of the metal in a current of oxygen at a moderate temperature, or by heating a mixture of a palladium salt with potassium carbonate. Prepared in the first manner it is a bluish-green, and by the second an amber-coloured mass, which yields a black powder. On strong ignition it yields the metal, and is reduced by hydrogen at the ordinary temperature with evolution of light and heat. If a palladious salt be precipitated with sodium carbonate, a dark-brown hydroxide, readily soluble in acids, is thrown down, whilst the anhydrous oxide dissolves only after long boiling.

The palladious salts, corresponding to this oxide, possess a green, red, or brown colour, and have an astringent, but not metallic, taste.

Palladium Dioxide is obtained as a black powder by boiling palladdiammonium chloride with caustic soda, and readily yields the monoxide on heating. If the above double salt be dissolved in cold caustic soda, a yellowish-brown hydroxide separates out on standing in the form of a gelatinous precipitate, which is readily soluble in acids. Solutions of the palladic salts are probably thus formed, but the simple salts have not been isolated, as they readily pass into the palladious salts. They form, however, crystalline double salts.

Palladium and Hydrogen.

609 *Palladium Hydride*, Pd_2H (?).—This substance, discovered by Graham,[1] is formed by passing hydrogen over metallic palladium heated to redness, or by bringing the metal in

[1] *Phil. Mag.* 1866, **32**, 516.

contact with nascent hydrogen, the formation of the compound being accompanied by evolution of heat.

The amount of hydrogen absorbed by the metal varies considerably, as already mentioned in vol. i. p. 137, but Troost and Hautefeuille[1] believed that they had evidence of the existence of the definite compound Pd_2H, which however Hoitsema[2] was unable to confirm.

The specific gravity of the product corresponding to the above formula is 11·06, and on exposure to the air the compound sometimes becomes heated from absorption of oxygen and formation of water. As a rule, however, it does not undergo alteration either in the air or in a vacuum at the ordinary temperature, although it gives up its hydrogen on ignition. The specific gravity of palladium hydride is less than that of the metal, hence expansion must occur in the formation of the compound. This expansion can be shown in several ways. One of the most striking is to fix two palladium wires horizontally through the edges of a thin electrolytic trough with parallel glass sides. The trough is then filled with acidulated water, placed in the focus of the oxyhydrogen or electric light, and the image of the wires thrown on the screen. A current of electricity is now allowed to pass through the cell, when a singular bending of the palladium wire from which the hydrogen is evolved is noticed. If the current be reversed this wire first returns to its original horizontal position, and then bends to the opposite side, whilst the other wire is deflected in the former direction; the explanation of this double bending being that first one side, and then the other side of the wire becomes saturated with, or loses the hydrogen.[3]

If one side of a piece of palladium foil be saturated electrolytically with hydrogen, then taken out of the liquid, washed and dried, and afterwards ignited, it becomes so bent that it has almost the appearance of having been rolled up into a coil.

The arrangement shown in Fig. 183 is that proposed by Wöhler[4] for exhibiting the decomposition of palladium hydride by heat and the reabsorption of the hydrogen on cooling.

The U-tube (*a*) dipping in boiling water contains the spongy palladium, over which a current of hydrogen is passed for half an hour from the cylindrical generator on the right of the figure.

[1] *Compt. Rend.* 1874, **78**, 686. [2] *Zeit. phys. Chem.* 1895, **17**, 1.
[3] Poggendorff, *Ber.* 1869, **2**, 74; also Dewar, *Phil. Mag.* 1874 [4], **47**, 334.
[4] *Annalen*, 1876, **184**, 128.

The water-bath is then removed and the tube allowed to cool in the current of hydrogen. The stop-cock (*d*) is now shut, and the tube (*a*) placed in communication with the tube (*b*). This latter dips in the cylinder and is bent up at the lower end into the tube (*c*). The tube (*a*) is next heated with a flame, when the cylinder soon becomes filled with hydrogen, and on allowing the spongy metal to cool, a rapid absorption of the hydrogen occurs. The experiment can, of course, be repeated as often as is required.

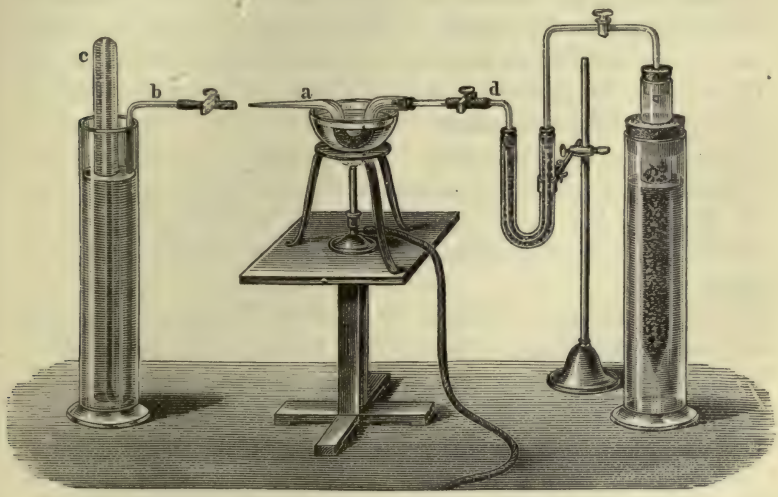


FIG. 183.

PALLADIUM SALTS.

610 *Palladious Chloride*, $PdCl_2$, is obtained by heating palladious sulphide, PdS, in dry chlorine, when it is obtained partly as a rose-red sublimate and partly in the form of garnet-red crystals, which dissolve slowly but completely in water. It is prepared in solution by the simultaneous action of chlorine and hydrochloric acid on the metal. On evaporation over caustic lime brown-red crystals, having the composition $PdCl_2 + 2H_2O$, are deposited. These lose water when gently heated, the anhydrous chloride remaining as a brownish-black mass which melts easily without decomposition and is reduced by hydrogen in the cold. At a red-heat it fuses and loses half of its chlorine, forming the monochloride, PdCl, which, on cooling, solidifies to a reddish-

brown crystalline mass yielding a light-red powder which is very deliquescent. The aqueous solution partially decomposes with separation of metal.

Palladious chloride forms double chlorides with other chlorides; thus:

Potassium Chloropalladite, K_2PdCl_4, is obtained by dissolving the metal in hydrochloric acid to which nitre has been added, or by evaporating the solution of the metal in aqua-regia until the excess of acid has been driven off, and then adding chloride of potassium. It may also be prepared by the ignition of potassium chloropalladate. It is easily soluble in water, less so in alcohol, and crystallises in four-sided prisms, which when viewed in the direction of the primary axis have a red, but in other directions exhibit a light-green, colour.

Ammonium Chloropalladite, $(NH_4)_2PdCl_4$, is obtained by evaporating a solution of palladium chloride with sal-ammoniac. It forms either bronze-yellow prisms exhibiting a play of different colours, or needles, and dissolves in water with a dark-red colour.

Palladic Chloride, $PdCl_4$, is obtained by dissolving the metal in concentrated aqua-regia. The brown solution doubtless contains *chloropalladic acid*, H_2PdCl_6, corresponding to chloroplatinic acid.

Potassium Chloropalladate, K_2PdCl_6, is obtained by adding potassium chloride to a solution of the metal in an excess of aqua-regia, and gently evaporating. It is also prepared by precipitating a solution of palladious chloride, saturated with chlorine, with an excess of potassium chloride. It forms cinnabar-red or brownish-red octahedra showing the faces of the cube. These dissolve in hot dilute hydrochloric acid without decomposition, but are not soluble in water containing the chlorides of the alkali metals, or in alcohol.

Ammonium Chloropalladate, $(NH_4)_2PdCl_6$, is a bright red crystalline powder consisting of microscopic octahedra. It is obtained by precipitating a solution of the chloride, saturated with chlorine, by sal-ammoniac. On treating the solution with an excess of ammonia a violent evolution of nitrogen takes place, ammonium chloropalladite being formed:

$$3(NH_4)_2PdCl_6 + 2NH_3 = 3(NH_4)_2PdCl_4 + 6HCl + N_2.$$

Palladious Bromide, $PdBr_2$, is obtained by treating the metal with bromine hydrate and nitric acid, and forms a chestnut-brown

mass which dissolves in hydrobromic acid but not in water. *Potassium bromopalladite*, K_2PdBr_4, crystallises in lustrous reddish-brown needles which are stable in the air.

Palladious Iodide, PdI_2, is obtained by precipitating the chloride with potassium iodide as a black flocculent precipitate which when dried in the air forms a deliquescent mass exhibiting a conchoidal fracture. It dissolves slowly in hydriodic acid and readily in a solution of potassium iodide, imparting to this a wine-red colour. When heated to 100° it begins to give off iodine and decomposes completely at temperatures between 330° and 360°. The solution in potassium iodide yields on evaporation blackish-green deliquescent cubes.

Palladium Subsulphide, Pd_2S, is obtained by fusing ammonium chloropalladite with sodium carbonate, sulphur, and sal-ammoniac. A green molten mass is thus obtained which crystallises on cooling and exhibits a metallic fracture. It is only slowly attacked by aqua-regia.

Palladium Monosulphide, PdS, is formed with incandescence by heating the metal in the vapour of sulphur. It is a bluish-white hard metallic lustrous mass with a laminated fracture, which only oxidises slowly in the air. A black precipitate is formed by passing sulphuretted hydrogen through a solution of a palladious salt, which is generally supposed to be palladious sulphide, but according to Petrenko-Kritchenko[1] this always contains more sulphur than is required by the formula PdS.

Palladium Disulphide, PdS_2.—When the foregoing compound is fused with sodium carbonate and sulphur, *sodium thiopalladate*, Na_2PdS_3, is formed. This crystallises in reddish-brown needles, having a slightly metallic lustre. It is decomposed by hydrochloric acid with formation of the disulphide, which is a crystalline dark brown powder easily soluble in aqua regia. When heated in carbon dioxide it is first converted into the monosulphide, and at a higher temperature into the subsulphide.

Sodium Palladiosulphite, $Na_6Pd(SO_3)_4+2H_2O$, is obtained as a white crystalline precipitate by adding caustic soda to a solution of the chloride which has been saturated with sulphur dioxide.

Palladious Sulphate, $PdSO_4+H_2O$, is obtained by dissolving the hydroxide in sulphuric acid, or by dissolving the metal in the same solvent with the addition of nitric acid. It forms indistinct olive-green deliquescent crystals which are decom-

[1] *Zeit. anorg. Chem.* 1893, **4**, 247.

posed by water with formation of a basic salt, $PdSO_4+7Pd(OH)_2$, as a brown insoluble powder.

Potassium Palladionitrite, $K_2Pd(NO_2)_4$, is obtained on addition of potassium nitrite to a hot solution of potassium chloropalladite, as a pale yellow crystalline powder.

Palladious Nitrate, $Pd(NO_3)_2$, is formed by dissolving the metal or the oxide in nitric acid. It crystallises in long brownish-yellow rhombic prisms which probably contain water of crystallisation, and are very deliquescent. A brown powder of $Pd(NO_3)_2+3Pd(OH)_2$ is formed on the addition of water to the solution.

Palladious Cyanide, $Pd(CN)_2$, is obtained as a pale yellow precipitate on addition of mercuric cyanide solution to a solution of a palladious salt, which must contain no free acid and should not be too dilute. On solution in potassium cyanide and evaporation, transparent thin rhombic prisms of *potassium palladocyanide*, $K_2Pd(CN)_4 + 3H_2O$, or small tables of $K_2Pd(CN)_4+H_2O$ are obtained. The cyanide is also soluble in acids and in ammonia, and the latter solution yields *palladosammonium cyanide*, $Pd(NH_3)_2(CN)_2$, in needles or in crystalline scales possessing a pearly lustre.

Ammoniacal Palladium Compounds.

611 These have been chiefly investigated by Hugo Müller,[1] and are formed by the action of ammonia on palladious salts. Of these, two bases exist to which he gave the names palladamine and palladdiamine but which were afterwards termed palladammonium hydroxide, and palladdiammonium hydroxide.

These compounds are doubtless closely analogous in constitution to the corresponding platinum compounds (q.v.).

Dihydroxy-diammine Palladium or *Palladammonium Hydroxide*, $[(OH)_2(NH_3)_2Pd]$, is obtained by the decomposition of the sulphate with baryta-water, or of the chloride with oxide of silver and water. The yellow solution thus obtained when dried over sulphuric acid yields a crystalline ochre-yellow mass. The solution has a strongly alkaline reaction, readily absorbs carbon dioxide, and has a bitter taste, producing insensibility on that portion of the tongue which has been in contact with it. It precipitates the salts of copper and silver and decomposes ammonium salts on boiling.

[1] *Annalen*, 1853, **86**, 341.

Dichloro-diammine Palladium or *Palladammonium Chloride*, $[Cl_2(NH_3)_2Pd]$, is obtained by the addition of an excess of ammonia to palladious chloride and either evaporating, or, better, precipitating the salt by means of hydrochloric acid. It forms fine yellow needles which consist of glistening octahedra placed one upon the other, and is almost insoluble in water.

Tetramminepalladious Hydroxide or *Palladdiammonium Hydroxide*, $[(NH_3)_4Pd](OH)_2$, is obtained by the decomposition of the sulphate with baryta-water. It is a colourless crystalline mass, the aqueous solution of which has a strong alkaline reaction, precipitates the salts of copper, iron, cobalt, nickel, and aluminium, but not those of silver, and decomposes ammoniacal salts.

Tetramminepalladious Chloride or *Palladdiammonium Chloride*, $[(NH_3)_4Pd]Cl_2$, is formed by the repeated evaporation of palladious chloride with ammonia. It crystallises in large, colourless, four-sided, monosymmetric prisms, and is easily soluble in water.

Besides these there are known several other palladammonium salts which all crystallise well.

Detection and Estimation of Palladium.

612 The two most characteristic reactions of palladium are (1) the precipitation of its hydrochloric acid solution by cyanide of potassium, the yellowish-white cyanide of palladium being thrown down, soluble in both hydrochloric acid and ammonia; and (2) the production of a black precipitate of palladious iodide, insoluble in hydrochloric acid, when potassium iodide is added to a palladium solution. By these reactions it may be separated from all metals, with the exception of copper, and this may be previously removed, according to Wöhler, by precipitation as cuprous thiocyanate after saturation with sulphur dioxide.

Palladium is determined *quantitatively* as the metal, usually obtained by the ignition of the cyanide.

Atomic Weight of Palladium.—Until the year 1889 the only determination of the atomic weight of palladium was that of Berzelius, who obtained the number 106 by the analysis of potassium chloropalladite. Since 1889 the atomic weight has been redetermined by several investigators, but the different results

vary considerably. Keiser[1] by the determination of the palladium in palladammonium chloride found the number 105·82, and from a later redetermination by the same method using very carefully purified material Keiser and Breed[2] gave the number 105·72. Bailey and Lamb[3] by the same method found the number 104·93, and a value closely agreeing with this, viz. 104·91, was obtained by Joly and Leidié[4] by the analysis of potassium chloropalladite. Keller and Smith,[5] on the other hand, from the electrolytic determination of the metal in palladammonium chloride obtained the much higher number 106·37 (O = 15·88).

[1] *Amer. Chem. J.* 1889, **11**, 398.
[2] *Amer. Chem. J.* 1894, **16**, 20.
[3] *Journ. Chem. Soc.* 1892, i. 745.
[4] *Compt. Rend.* 1893, **116**, 146.
[5] *Amer. J. Sci.* 1892, **44**, 423.

SUB-GROUP (*c*) THE PLATINUM GROUP.

Osmium. Iridium. Platinum.

THESE metals are distinguished by their high specific gravity and melting point. Both osmium and iridium become oxidised when heated in the air or in oxygen, whereas platinum remains quite unaltered. Osmium alone forms a tetroxide, thus resembling ruthenium.

The tendency to form complex salts is exceedingly strongly marked, and with the exception of the sulphides and halogen derivatives, very few simple salts are known. Such as are known have the general formulæ MR_2, MR_3, and MR_4, corresponding to the basic oxides MO, M_2O_3, and MO_2, but the series MR_3 is scarcely represented among the platinum compounds. The most important of the series of the complex salts are the halogen acids and their derivatives, such as K_2PtCl_4, $K_3Ir_2Cl_6$, and K_2OsCl_6, the complex nitrites, such as $K_3Ir_2(NO_2)_6$ and $K_3Pt(NO_2)_6$, the complex cyanides and thiocyanates, such as $K_2Pt(CN)_4$ and $K_2Pt(SCN)_4$, the sulphites, and above all the ammoniacal derivatives.

OSMIUM, 189·3.

613 In 1803 Smithson Tennant investigated the metallic residue which remains when platinum ores are dissolved, and this he believed to contain a new metal. At the same time Descotils, as well as Fourcroy and Vauquelin, examined the same subject, and also came to the conclusion that the solution contained a peculiar metal. However, in 1804 Tennant[1] proved that the platinum residues contained two new metals, to one of which he

[1] *Phil. Trans.* 1804, 411.

gave the name of iridium, on account of the varying colour of its salts, and to the other the name osmium (ὀσμή, a smell), because of the peculiar odour which its volatile oxide possesses. Osmium is found in platinum ores in the form of an alloy with iridium, known as osmiridium, which is described under iridium (p. 1115). It may be easily separated from the other members of the platinum group by means of its property of combining directly with oxygen to form a very volatile tetroxide, OsO_4. This compound is obtained, in a more or less pure state, in the course of the preparation of the other platinum metals, and especially of ruthenium (see p. 1081). The solution thus obtained may be precipitated with ammonia and ammonium sulphide, and the precipitated sulphide mixed with sodium chloride, and heated in a slow current of chlorine. The mass when lixiviated yields sodium chlorosmate, Na_2OsCl_6, and from this solution ammonium chlorosmate is thrown down by sal-ammoniac. This is next washed with sal-ammoniac solution, and then heated in a covered crucible, when spongy osmium is obtained. The sulphide may also be simply heated in a well-covered carbon crucible to the temperature of the melting point of nickel.

Pure osmium was obtained by Deville and Debray,[1] by passing the vapour of the pure tetroxide mixed with carbon monoxide and carbon dioxide through a red-hot porcelain tube. Thus prepared, the metal assumes the form of an amorphous powder, which is converted into the crystalline variety when fused with from three to four times its weight of tin in a charcoal crucible, the crystalline alloy treated with hydrochloric acid, and the residue heated in a current of hydrochloric acid gas.

The crystalline form of osmium is either that of the cube or of a very obtuse rhombohedron. The crystals possess a bluish-white colour with violet lustre, are harder than glass, and possess a specific gravity of 22·477. Hence osmium is the heaviest of known bodies. Osmium has not yet been fused. When it is heated up to the temperature at which iridium is fully melted it evaporates and is deposited in the form of a black powder on a cold surface held in the vapour, whilst it takes fire in the air, and forms the tetroxide.

The experiment of volatilising osmium in the oxyhydrogen furnace is one accompanied by great danger. Deville, who performed the operation twice, was rendered almost blind for

[1] *Compt. Rend.* 1876, **82**, 1076.

twenty-four hours by having accidentally become exposed to the vapour of the tetroxide. This substance produces the most violent pain and inflammation of the conjunctiva, and vision is permanently injured by the subsequent reduction of a film of metallic osmium.[1]

Crystalline osmium is not attacked even by aqua-regia, and must be brought into solution by fusion with caustic soda and potassium nitrate, or barium peroxide and nitrate; the amorphous metal, on the other hand, is readily dissolved by fuming nitric acid, more slowly by aqua-regia.

Osmium is not used in the arts, but the alloy of osmiridium, which is not attacked by acids, is employed for tipping gold pens, and, inasmuch as it is unoxidisable and non-magnetic, it has been employed for the bearings of the mariner's compass.

COMPOUNDS OF OSMIUM.

Osmium and Oxygen.

614 The following oxides are known;

Osmium Monoxide,	OsO.
Osmium Sesquioxide,	Os_2O_3.
Osmium Dioxide,	OsO_2.
Osmium Tetroxide,	OsO_4.

In addition to these, osmic acid, H_2OsO_4, and its salts are known, but the corresponding oxide has not been prepared.

The first three of these oxides act as feeble basic oxides, but very few of their salts have as yet been examined, only the sulphite and chloride corresponding to the monoxide, and double chlorides of the formula $3M_1Cl + OsCl_3$, corresponding to the sesquioxide, being known. The chloride, $OsCl_4$, has however been prepared along with double chlorides corresponding to the derivatives of chloroplatinic acid. Osmic acid forms a series of osmates with the alkali metals, whilst the tetroxide yields a neutral solution in water, and yields salts with neither acids nor bases.

Osmium Monoxide, OsO, is obtained when the corresponding sulphite mixed with sodium carbonate is ignited in a current

[1] *Ann. Chim. Phys.* 1859 [3], **56**, 400.

of carbon dioxide. It is a greyish-black powder insoluble in acids.

Osmium Sesquioxide, Os_2O_3, is a black powder insoluble in acids obtained by heating its salts with sodium carbonate in a current of carbon dioxide. Deville and Debray obtained this oxide in copper-red scales, together with the metal, by the reduction of the tetroxide. A brownish-red *hydroxide* is precipitated by alkalis from solutions of the chlorosmites of the alkali metals.

Osmium Dioxide, OsO_2, is obtained from its salt in a similar way to the foregoing oxides. It is likewise formed when its hydroxide is heated in a current of carbon dioxide. Prepared in this way it forms masses having a coppery lustre. It does not decompose in absence of air even at a red-heat, but when mixed with combustible bodies it deflagrates on heating.

Osmium Tetrahydroxide, $Os(OH)_4$, is produced when caustic potash is added to a solution of potassium chlorosmate, and when the aqueous solution of the tetroxide is mixed with alcohol or other reducing agent, or when potassium osmate is exposed to sunlight or treated with nitric acid:

$$2K_2OsO_4 + 4HNO_3 = Os(OH)_4 + OsO_4 + 4KNO_3.$$

According to Moraht and Wischin, these last two forms really consist of osmic acid. It is a black precipitate which dries up to a heavy brown mass having a coppery lustre. When freshly precipitated it is tolerably soluble in hydrochloric acid, and when heated in nitrogen to 200° it is converted into $OsO(OH)_2$. Only a few of its salts have been accurately examined, as they rapidly undergo decomposition in solution.

Osmium Trioxide, OsO_3, is unknown, but, according to Moraht and Wischin,[1] the substance obtained when a solution of potassium osmate is exposed to sunlight or treated with nitric acid is in reality *osmic acid*, H_2OsO_4. After drying over phosphoric oxide it forms a black powder, which oxidises in the air to the tetroxide, and readily reacts with sulphuretted hydrogen, forming an *oxysulphide*, $Os_2O_2S_2 + H_2O$. It dissolves in nitric acid to form the tetroxide, and in hydrochloric and hydrobromic acids to form mixtures of salts.

Potassium Osmate, $K_2OsO_4 + 2H_2O$, is obtained on the addition of alcohol or other reducing agent to the solution of the

[1] *Zeit. anorg. Chem.* 1893, **3**, 153.

tetroxide in caustic potash. The liquid then becomes of a fine red colour, and when it is sufficiently concentrated the salt separates out as a crystalline powder. When slowly crystallised it forms octahedra which according to their size are of a garnet-red or almost black colour. They possess a sweet astringent taste, and do not undergo change on exposure to dry air, but both in solution and in moist air they decompose, especially on addition of an acid, with formation of tetroxide and lower oxides.

The *sodium* salt crystallises less easily, and yields an aqueous solution having a rose-red colour, from which barium chloride precipitates $BaOsO_4$ as an amorphous green flocculent precipitate, which after a while changes to black shining prismatic crystals.

Osmium Tetroxide or *Perosmic Anhydride* (commonly called osmic acid), OsO_4.—Very finely-divided metallic osmium oxidises slowly at the ordinary temperature, and at about 400° takes fire with formation of the above oxide. The denser the metal the higher is the temperature needed for oxidation. Osmium tetroxide may also be obtained by heating the metal in a current of steam, and also by dissolving the lower oxides or the metal in nitric acid or aqua-regia. These reagents however do not attack the metal after it has been strongly ignited. Osmium tetroxide sublimes in transparent glistening needles which become soft and may be moulded in the hand like wax, and melt at a lower temperature than this substance. They begin to sublime at a very moderate heat, and the fused oxide boils at 100°, yielding a colourless vapour having a specific gravity of 8·89, which is slightly greater than the calculated value. The crystals readily dissolve in water, forming a colourless liquid which does not redden litmus paper, and possesses a caustic and burning taste. It has a most powerful penetrating smell, somewhat analogous to that of chlorine and iodine. A very small quantity of vapour mixed with air attacks the lungs, giving rise to very serious inflammation of the mucous membrane. As an antidote to the effects of the osmic acid Claus recommends the inhalation of sulphuretted hydrogen, which however must be cautiously employed. Osmium tetroxide also acts violently on the skin, causing a painful eruption which can be removed by the use of sulphur baths. The vapour also acts, as has been stated, most violently on the eyes, and may produce most serious consequences.[1]

[1] Deville and Debray, *Ann. Chim. Phys.* 1859 (3), **56**, 400; *Compt. Rend.* 1874, **78**, 1509.

When heated on red-hot charcoal it deflagrates like nitre. It is easily converted into lower oxides by reducing substances, and its alkaline solution when boiled with a salt of formic acid yields a blue precipitate. If osmium tetroxide be dissolved in alcohol or ether, the whole of the osmium is precipitated as the tetrahydroxide on standing for twenty-four hours. Sulphur dioxide colours the aqueous solution yellow, then brown, green, and at last indigo-blue.

It is used in microscopic work for obtaining preparations, the oxide being reduced to metallic osmium.

Osmium and the Halogens.

615 *Osmium Dichloride,* $OsCl_2$, is obtained in very small amount by heating osmium in chlorine, as a brownish-black powder which forms a dark violet-coloured unstable solution in water.

Osmium Trichloride, $OsCl_3$, in the free state is not known with certainty. Its double salts with potassium and ammonium chlorides have however been prepared.

Potassium Chlorosmite, $K_3OsCl_6+3H_2O$, is obtained by adding ammonia to a solution of osmium tetroxide in caustic potash, and saturating the liquid, as soon as it has become yellow, with hydrochloric acid. On evaporation, the above salt separates out together with potassium and ammonium chloride. This latter can be readily separated mechanically. It forms dark-red crystals which effloresce in the air and become pink. It dissolves in water, yielding a cherry-red coloured solution, possessing first a strongly astringent, and then a sickly sweetish taste.

Ammonium Chlorosmite, $2(NH_4)_3OsCl_6+3H_2O$.—In order to prepare this salt sulphuretted hydrogen is passed into a hydrochloric acid solution of the tetroxide until it has become red. The liquid is then evaporated with sal-ammoniac, when fine red crystals are deposited resembling the potassium salt.

Osmium Tetrachloride, $OsCl_4$, is obtained by heating the metal in dry chlorine. It forms a red sublimate which dissolves in water, yielding a yellow solution; and this on dilution with more water attains a green tint. On standing the solution becomes colourless with separation of lower oxides, whilst hydrochloric acid and osmium tetroxide remain in solution.

Potassium Chlorosmate, K_2OsCl_6, is obtained by gently heating a mixture of the finely-divided metal with potassium chloride in a current of chlorine, and also by evaporating the hydrochloric acid solution of the tetroxide with potassium chloride. It crystallises in dark-brown glistening octahedra, which yield a cinnabar-red powder, and dissolve in water with a yellow colour. Alcohol precipitates the compound from this solution in the form of a red crystalline powder.

Sodium Chlorosmate, $Na_2OsCl_6+2H_2O$, is obtained in a similar way, and crystallises in long orange-coloured prisms which are easily soluble in water and alcohol.

Ammonium Chlorosmate, $(NH_4)_2OsCl_6$, is obtained by the addition of powdered sal-ammoniac to a solution of the sodium salt. It is then deposited as a red crystalline powder, crystallising from dilute solution in brown octahedra.

Osmium and Sulphur.

616 Metallic osmium burns when heated in sulphur vapour, and sulphuretted hydrogen throws down a dark-yellow sulphide of osmium from the hydrochloric acid solution of the oxide. This is slightly soluble in water, giving rise to a dark-yellow solution, and easily dissolves in nitric acid.

Osmium Tetrasulphide, OsS_4, is thrown down as a brown precipitate when sulphuretted hydrogen is passed through an aqueous solution of osmium tetroxide. It is insoluble in alkalis and the sulphides of the alkali metals.

Osmium Sulphite, $OsSO_3$.—In order to prepare this salt, sulphur dioxide is led into an aqueous solution of the peroxide, and glauber-salt added to the blue liquid. The dark-blue gelatinous precipitate, after washing, is dried and yields a powder which is unalterable in the air, and which on trituration exhibits a metallic silvery lustre. If the blue solution be treated with caustic potash a blackish-blue precipitate of hydroxide is obtained, which on exposure to air absorbs oxygen as rapidly as ferrous hydroxide.

Potassium Osmium Sulphite, $H_2K_6Os(SO_3)_5+4H_2O$, is obtained by heating the solution of potassium chlorosmite with potassium sulphite. It is a crystalline pale rose-red precipitate.

Osmium and Nitrogen.

617 Osmium like the other metals of this sub-group, forms ammoniacal compounds, but these have not as yet been at all fully investigated. It also forms a characteristic compound termed osmiamic acid, which is probably analogous to the nitroso-derivatives of ruthenium.

Osmosammine Hydroxide, $Os(NH_3)_2(OH)_2$, is obtained by dissolving the tetroxide in an excess of concentrated ammonia, and heating the reddish-yellow solution in a closed vessel to 50°, when a black precipitate is formed. The flask is then opened and the solution evaporated at a low temperature until the excess of ammonia has been driven off. The base is thus obtained in the form of a blackish-brown powder, which when heated decomposes with rapid evolution of gas. With acids it forms amorphous salts.

Osmyldiammine Chloride, $Os(NH_3)_4O_2Cl_2$, is obtained on the addition of sal-ammoniac to a solution of potassium osmate, in the form of a yellow crystalline precipitate easily soluble in water, the solution soon undergoing decomposition.[1]

Osmiamic acid, $OsNO_3H$.—Potassium osmiamate is formed by the action of ammonia on the tetroxide, especially in the presence of potash, the potassium salt being more stable than the ammonium compound. It was at first supposed[2] that this substance had the formula $K_2N_2Os_2O_5$ and was formed according to the equation

$$2OsO_4 + 2NH_3 + 2KOH = K_2N_2Os_2O_5 + 4H_2O + O.$$

According to Joly,[3] however, the salt has the formula $KNOsO_3$, and no oxygen is liberated, the reaction being

$$OsO_4 + KOH + NH_3 = KNOsO_3 + 2H_2O.$$

The free acid is obtained by decomposing the barium salt with dilute sulphuric acid, or the silver salt with hydrochloric acid. The light-yellow solution remains in the dilute state without change for some time. In the concentrated condition, however, it decomposes with evolution of gas and separation of a brown powder.

[1] See also Wolcott Gibbs, *Amer. J. Sci.* **3**, 233.

[2] Fritzsche and Struve, *Petersb. Acad. Bull.* **6**, 81.

[3] *Compt. Rend.* 1891, **112**, 1442.

It is probably to be regarded as an anhydride of $Os(NO)(OH)_3$, which is analogous to the ruthenium compounds $Ru(NO)Cl_3$, &c.

Potassium Osmiamate, $KNOsO_3$, forms orange-yellow quadratic pyramids, which dissolve slowly in cold, and more readily in hot water, and on recrystallisation become dark-coloured, owing to partial decomposition. It decomposes when heated with loss of nitrogen.

Crystalline salts of sodium, barium and silver are also known.

Osmium and Carbon.

618 Osmium forms a series of osmocyanides which correspond closely in composition and in their properties to the ferrocyanides. The most important of these compounds are the following:

Osmocyanic Acid, $H_4[Os(CN)_6]^{iv}$, is deposited in the form of white scales on the addition of fuming hydrochloric acid to a solution of the potassium salt. These are easily soluble in alcohol, and crystallise out from the alcoholic solution on the addition of ether in colourless glistening transparent hexagonal prisms. Its aqueous solution has an acid reaction, and from it osmous cyanide, $Os(CN)_2$, separates out as a dark-violet precipitate.

Potassium Osmocyanide, $K_4[Os(CN)_6]+3H_2O$, is obtained by adding potassium cyanide to an alkaline solution of osmium tetroxide, evaporating the filtered solution and heating the residue. It crystallises from hot water, in which it is easily soluble, in yellow quadratic tables, which when heated give off water and become colourless. Its solution yields a light-blue precipitate with ferrous salts, which becomes darker-coloured on exposure to air, and when treated with nitric acid it is converted into a fine violet-coloured powder, which is also obtained by precipitating the potassium salt with ferric chloride. After drying this forms a fragile mass having a copper-red colour, and when boiled with caustic potash it yields ferric hydroxide and potassium osmocyanide.

Barium Osmocyanide, $Ba_2[Os(CN)_6]+3H_2O$, is formed when the iron precipitate is boiled with baryta-water. It crystallises in small yellowish-red transparent rhombic prisms, which are easily soluble in water and alcohol.

Potassium Barium Osmocyanide, $K_2Ba[Os(CN)_6]+3H_2O$, is

obtained by mixing hot solutions of the potassium and barium salts. On cooling small yellow oblique rhombohedra are deposited, which are difficultly soluble in cold water.

Detection and Estimation of Osmium.

619 The presence of this metal may be most easily detected by the formation of the volatile strongly-smelling tetroxide. Sulphuretted hydrogen throws down a precipitate of the sulphide insoluble in sulphide of ammonium. If a solution contain a mixture of the platinum metals, and other metals precipitable by sulphuretted hydrogen, this gas is passed into the hot solution so long as a precipitate is formed. This is then washed and warmed with yellow sulphide of ammonium, when platinum, iridium, gold, &c., dissolve. The filtrate is then acidified with hydrochloric acid, the precipitate fused with sodium carbonate and sodium nitrate, and the fused mass lixiviated with water, the residue being treated according to the method described under platinum (see p. 1154). In this way the iridium is obtained together with platinum and gold, and these may be readily separated. The portion insoluble in sulphide of ammonium is then fused with caustic potash and potassium chlorate, and treated with water in order to dissolve the potassium salts of ruthenic and osmic acids. The solution is carefully neutralised with nitric acid in order to separate the black oxide of ruthenium, and the filtrate distilled with nitric acid, when the volatile osmium tetroxide passes over. The residue insoluble in water is gently ignited in a current of hydrogen, treated with dilute nitric acid, when palladium and rhodium remain behind, and these are separated by aqua-regia, in which the latter metal is insoluble.

Osmium is usually estimated *quantitatively* as the metal. It is separated from other metals as the volatile tetroxide, the vapours of which, in order to avoid loss, are passed into caustic potash; alcohol is added to the distillate in order to form potassium osmate, and the solution then treated with sal-ammoniac and the precipitated osmyldiammine chloride ignited in hydrogen, when the metal is obtained.

The atomic weight of osmium was determined by Berzelius in 1828 in a similar way to that of platinum, and he obtained the number 197·6, whilst Frémy,[1] in 1844, by converting the

[1] *Ann. Chim. Phys.* 1844 (3), **12**, 514.

metal into the tetroxide obtained the number 198·2. According to these determinations the atomic weight of osmium appeared to be greater than that of iridium, whereas the analogies of the metal with ruthenium seemed to indicate that it should precede iridium in the periodic system, just as ruthenium precedes rhodium. In 1888 Seubert[1] redetermined the atomic weight by analysing pure potassium and ammonium chlorosmates and obtained the number 190·1, whilst in 1891 from a later[2] and more concordant series of experiments he obtained the still lower number 189·3, which represents the most probable value (O = 15·88).

IRIDIUM. 191·7.

620 The history of the discovery of this metal has already been described under osmium.

Iridium is found in the platinum ores in considerable quantity in the form of the alloys platiniridium and osmiridium. The first of these occurs in grains, and often in small cubes with rounded edges; the second usually in flat, irregular grains, and occasionally in hexagonal prisms. The composition of these minerals is shown in the following analyses:

	Platiniridium.		Osmiridium.			
	Urals.	Brazil.	Urals.	New Granada.	Cali-fornia.	Austra-lia.
Iridium . .	76·85	27·79	55·24	57·80	53·50	58·13
Osmium .	—	—	27·23	35·10	43·40	33·46
Platinum .	19·64	55·44	10·08	—	—	—
Rhodium .	—	6·86	1·51	0·63	2·60	3·04
Ruthenium.	—	—	5·85	6·37	0·50	5·22
Palladium .	0·89	0·49	trace	—	—	—
Iron . . .	—	4·14	trace	0·10	—	—
Copper . .	1·78	3·10	trace	0·06	—	0·15
	99·16	97·82	99·91	100·06	100·00	100·00

Iridium is usually prepared from the alloys described above, which are left behind when platinum ores are treated with

[1] *Ber.* 1888, **21**, 1839. [2] *Annalen*, 1891, **261**, 257.

aqua-regia. One of the most efficacious of the many methods[1] which have been proposed for the extraction of the metal, is that employed by Deville and Debray[2] in the production of the pure iridium required for the standard metre bars of platinum-iridium prepared for the International Commission on the Metrical System. The osmiridium is fused with zinc and heated until all the zinc evaporates, the porous residue being then powdered and ignited with barium nitrate, which converts the iridium into oxide and the osmium into barium osmate. The residue after extraction with water is boiled with nitric acid, which brings the iridium into solution, whilst the osmium is volatilised in the form of tetroxide. The iridium oxide is precipitated from the residual solution by baryta, dissolved in aqua-regia, and then thrown down as the double chloride of iridium and ammonium. This, on ignition, yields spongy iridium, containing small quantities of platinum, ruthenium, and a little rhodium. The metal is then ignited with potassium nitrate, and the mass treated with water, when potassium ruthenate dissolves. It is lastly fused with lead, the regulus obtained leaving, after treatment with nitric acid and aqua-regia, a residue of pure iridium.

After osmium and ruthenium, iridium is the most difficultly fusible of the platinum metals, and is slightly volatile. It possesses a white lustre, resembling that of polished steel. In the cold it is very brittle, but at a white-heat it is somewhat malleable. The specific gravity of the fused metal is 21·15, whilst that of the crystallised metal is 22·4. If the alcoholic solution of the sulphate be exposed to the sunlight the metal is deposited as an extremely fine impalpable black powder, which, when washed with hot water and dried, acts even more energetically in bringing about the combination of combustible gases than does platinum black. The smallest trace brought on to paper saturated with alcohol produces ignition, the metal at the same time being converted into a grey sponge. Spongy iridium is prepared by igniting the double chloride of iridium and ammonium. This oxidises when heated in the air, and when ignited becomes dense and lustrous, and then absorbs oxygen only slowly, whilst the coherent metal does not do so at all. Iridium black, as well as the coherent

[1] Wöhler, *Pogg. Ann.* 1833, **31**, 161; Claus, *Annalen*, 1858, **107**, 134; Gibbs, *Amer. J. Sci.* [2], **31**, 70; Matthey, *Proc. Roy. Soc.* 1879.

[2] *Compt. Rend.* 1874, **78**, 1502.

metal, when alloyed with much platinum, dissolves in aqua-regia. Pure massive iridium is, however, not attacked. When it is heated with acid potassium sulphate, or in presence of fused alkalis, it is oxidised, and it unites directly with chlorine at a dull red-heat. When the metal is held in the middle of a flame of alcohol it becomes covered with a black moss-like deposit, which has the composition IrC_4, and easily takes fire on exposure to the air. The metal is in this case penetrated throughout its mass with carbon, and becomes of a dark grey colour. The oxides are also converted into the carbide of iridium, with evolution of light and heat, when they are heated in gases or vapours containing carbon. The fused metal also dissolves carbon, which, however, separates out on cooling as graphite.

Iridium is sometimes used for pointing gold pens, and is first heated with phosphorus, which renders it more fusible and easy to work. The phosphorus is afterwards removed by heating the mass in a lime crucible.

It forms an alloy with 9 parts of platinum, which is extremely hard, as elastic as steel, perfectly unalterable in the air and capable of taking an exceedingly fine polish. This alloy has been employed in the production of standard metre bars and for making electrodes to be used in corrosive liquids. A similar alloy is used for the wires employed in high temperature pyrometers.

COMPOUNDS OF IRIDIUM.

621 Iridium forms two basic oxides, the sesquioxide Ir_2O_3 and the dioxide IrO_2 and two corresponding series of salts, the sesqui-salts, of the general formula IrR'_3 and the iridic salts IrR'_4. The halogen compounds form double salts with the corresponding alkali compounds, which must be looked upon as alkali salts of complex acids. Compounds in which the metal is divalent are also known, but have only been slightly investigated. Like the other members of this group, iridium forms numerous complex derivatives, the chief of which are the halogen derivatives just mentioned, the double cyanides and the ammoniacal derivatives.

Iridium and Oxygen.

622 *Iridium Sesquioxide*, Ir_2O_3, is formed when potassium chloriridate, K_2IrCl_6, is mixed with sodium carbonate and heated to dull redness:

$$2K_2IrCl_6 + 4Na_2CO_3 = Ir_2O_3 + 8NaCl + 4KCl + 4CO_2 + O.$$

The fused mass is washed with water containing sal-ammoniac, and the residue, after ignition to expel the sal-ammoniac, is treated with dilute acid in order to remove the small quantity of alkali. A bluish-black powder is thus obtained which begins to decompose when heated above 800°, and at temperatures somewhat above 1000° is completely resolved into oxygen and the metal.

Deville and Debray[1] have investigated this subject, observing the dissociation into metal and oxygen which the oxide undergoes when heated in a porcelain tube. At a temperature of 1139° the oxide rapidly gives off oxygen, and metallic iridium remains behind in the tube. The tension of dissociation (p. 110), that is, the tension of the liberated gas, at the several temperatures was found to be as follows:

T°	Tension.
823°	5 mm.
1003°	203 „
1112°	711 „
1139°	745 „

Iridium sesquioxide is reduced by hydrogen at the ordinary temperature. In the pure state it imparts to porcelain after firing a fine black colour, and when mixed with zinc oxide it yields a grey tint.

Iridium Trihydroxide, $Ir(OH)_3$, is obtained by a process similar to that employed for the preparation of the corresponding rhodium compound, which it closely resembles. If a small quantity of caustic potash be added to a solution of potassium chloriridite, and the solution allowed to stand in a closed bottle, a yellowish-green precipitate of the hydroxide falls down, which readily dissolves in alkalis and oxidises quickly in the air.

Iridium Dioxide, IrO_2, is a black powder obtained by heating the hydroxide in a current of carbon dioxide, and is said to be

[1] *Compt. Rend.*, 1878, **87**, 441.

formed when the metal is heated to bright redness in the air.[1] It is insoluble in acids.

Iridium Tetrahydroxide, $Ir(OH)_4$, is formed by the oxidation of the trihydroxide in the air, or by precipitating the tetrachloride with an alkali, as well as by boiling potassium iridate with ammonium chloride. It is a heavy indigo-blue powder which is almost insoluble in dilute sulphuric and nitric acids, but dissolves completely, though slowly, in hydrochloric acid. Its solubility, however, appears to depend on the method of preparation. On heating the indigo-blue solution it becomes green and then brown.

Potassium Iridate is obtained as a partially soluble bluish mass when iridium is ignited with potassium nitrate. Its composition is not definitely known.

Salts of Iridium.

623 *Iridious Chloride*, $IrCl_2$, is formed as a green insoluble mass when chlorine is passed over spongy iridium at a red heat, and when the tetrachloride is heated.

Iridium Trichloride, $IrCl_3$, is prepared by heating one of its double salts with sulphuric acid. If the mass be then thrown into water the chloride separates out as a light olive-green precipitate insoluble in acids and in alkalis. It is obtained in solution by treating the hydrochloric acid solution of the tetrahydroxide with sulphur dioxide until it has become green. It forms complicated derivatives with the chlorides of phosphorus and arsenic.[2]

Potassium Chloriridite, $K_3IrCl_6 + 3H_2O$, is best obtained from the corresponding chloriridate by heating it with sulphuretted hydrogen, and adding potassium chloride to the olive-green solution It forms very soluble green rhombic prisms, which readily effloresce. The sodium and ammonium salts are similar compounds of the formulæ,

$$Na_3IrCl_6 + 12H_2O \text{ and } (NH_4)_3IrCl_6 + H_2O.$$

Iridium Tetrachloride, or *Iridic Chloride*, $IrCl_4$, is obtained by dissolving the finely-divided metal in aqua-regia, or by the solution of the blue hydroxide in hydrochloric acid. When the solution is evaporated at a temperature not above 40°, a black

[1] Geisenheimer, *Compt. Rend.* 1890, **110**, 855.

[2] Geisenheimer, *Compt. Rend.* 1890, **110**, 1004, 1336.

mass is obtained which appears red in thin films, and which contains a small quantity of trichloride. The hydrochloric acid solution probably contains *chloriridic acid*, H_2IrCl_6, corresponding to the following compounds.

Potassium Chloriridate, K_2IrCl_6, is obtained by the addition of potassium chloride to the above hydrochloric acid solution. On evaporation small blackish-red regular octahedra are deposited. These are slightly soluble in cold, and more readily in hot water, but do not dissolve in a saturated solution of an alkali chloride or in alcohol.

Sodium Chloriridate, Na_2IrCl_6, is easily soluble in water, and crystallises in almost black tables or prisms, which are isomorphous with the corresponding platinum compound.

Ammonium Chloriridate, $(NH_4)_2IrCl_6$, is obtained by precipitating the acid solution of the chloride by sal-ammoniac, and dissolves in 20 parts of water. It is a dark cherry-red powder, consisting of small blackish-red octahedra.

Iridium Tribromide, $IrBr_3 + 4H_2O$. When the blue hydroxide is dissolved in hydrobromic acid, a blue liquid is obtained which loses bromine on evaporation and deposits small, light, olive-green, six-sided crystals, having the above composition. They dissolve readily in water but are not soluble in alcohol and lose their water of crystallisation at 100°. From the mother-liquor of this salt steel-grey needles of bromiridious acid, $H_3IrBr_6 + 3H_2O$, are deposited, having a metallic lustre by reflected light. These, when heated to 100°, lose water and are converted into a brownish-red mass which is easily soluble in water and alcohol. The solution decomposes carbonates with formation of bromiridites.

Potassium Bromiridite, $K_3IrBr_6 + 3H_2O$, forms long olive-green lustrous four-sided needles which effloresce on exposure, becoming light-green and opaque. They readily dissolve in water.

Ammonium Bromiridite, $2(NH_4)_3IrBr_6 + 3H_2O$, is obtained by reducing the corresponding bromiridate with sulphur dioxide and neutralising with ammonium carbonate. It crystallises in dark olive-green prisms, and is isomorphous with the corresponding rhodium salt, with which it crystallises in all proportions.

Iridium Tetrabromide, or *Iridic Bromide*, $IrBr_4$.—The blue hydroxide dissolves in hydrobromic acid, giving rise probably to *bromiridic acid*, H_2IrBr_6. This on evaporation with nitric acid leaves a blue deliquescent crystalline mass. It forms,

with the other bromides, well crystallised bromiridates, such as K_2IrBr_6, which crystallises in opaque, lustrous, blackish-blue regular octahedra.

Iridium Tetriodide, or *Iridic Iodide*, IrI_4, is obtained by boiling the hydrochloric acid solution of the chloride with potassium iodide. It forms a black powder, which yields, with the iodides of the alkali metals, well crystallised double compounds possessing a ruby-red colour.

Iridium Monosulphide, IrS.—The metal burns when ignited in sulphur vapour, giving rise to this compound, which resembles galena in its appearance.

Iridium Sesquisulphide, Ir_2S_3, is precipitated when sulphuretted hydrogen is passed into a solution of a salt of iridium sesquioxide. It is a brown powder, somewhat soluble in pure water, and slightly so in potassium sulphide, and nitric acid.

Iridium Disulphide, IrS_2, is formed when the powdered metal is heated with sulphur and sodium carbonate, and is formed by the action of sulphuretted hydrogen on lithium chloriridate at 4°. It is a brown powder, insoluble in nitric acid, and decomposes at 300° into its elements.[1]

Iridious Sulphite has not itself been prepared, but several double salts with sodium sulphite, such as $IrSO_3 + 3Na_2SO_3 + 10H_2O$ and $IrH_2(SO_3)_2 + 3Na_2SO_3 + 4H_2O$ have been described by Seubert,[2] who obtained them during the separation of iridium from rhodium according to Bunsen's method.

Iridium Sesquisulphite, $Ir_2(SO_3)_3 + 6H_2O$, is obtained when the hydroxide suspended in water is treated for some time with sulphur dioxide. This compound is found in solution whilst a brown basic salt remains undissolved. The solution is then evaporated, when the normal sulphite separates out in the form of a yellow crystalline precipitate which is scarcely soluble in water but readily dissolves in dilute acids.

Iridionitrites.—These compounds have been investigated by Gibbs.[3]

Hydrogen Iridionitrite, $H_3Ir(NO_2)_6 + H_2O$, forms light yellow, easily soluble needles.

Potassium Iridionitrite, $K_3Ir(NO_2)_6 + H_2O$, is obtained in greenish-yellow crystals, and, like the sodium compound of corresponding composition, is easily soluble in water. It decom-

[1] Antony, *Journ. Chem. Soc.* 1893, **2**, ii. 380.
[2] *Ber.* 1878, **11**, 1761. [3] *Ber.* 1871, **4**, 280.

poses when heated, yielding among other products iridium dioxide.[1]

When a solution of potassium chloriridate is boiled with an excess of potassium nitrite, a yellow crystalline powder having the composition $3K_3Ir(NO_2)_6 + K_3IrCl_6$ is obtained. This is but slightly soluble even in boiling water, and is not attacked by cold hydrochloric acid.

624 *Cyanogen Derivatives of Iridium.*—The chief of these are the iridicyanides, which resemble the ferricyanides, and have been investigated by Martius.[2]

Potassium Irido-cyanide, $K_4[Ir(CN_6)]^{iv}$, is obtained in colourless prisms when potassium ferrocyanide is gently ignited with iridium.

Iridicyanic Acid, $H_3[Ir(CN)_6]^{iii}$, is obtained by decomposing the barium salt with dilute sulphuric acid. It is very soluble in water and alcohol, less so in ether, and is deposited from solution in crystalline crusts. It possesses an acid reaction and has an unpleasant taste, and from its solutions hydrochloric acid precipitates green iridic cyanide.

Potassium Iridicyanide, $K_3[Ir(CN)_6]$, is obtained by heating the metal with potassium ferrocyanide, or by fusing ammonium chloriridate with potassium cyanide, and also by the decomposition of the barium salt with potassium sulphate. It crystallises in colourless quadratic prisms which are easily soluble in water, but insoluble in alcohol. It is a very stable body, which is not attacked when heated in chlorine or in hydrochloric acid gas.

Barium Iridicyanide, $Ba_3[Ir(CN)_6]_2 + 18H_2O$.—In order to prepare this compound the crude potassium salt is precipitated with copper sulphate, and the precipitate decomposed with baryta water. It forms hard, transparent, probably quadratic crystals, which effloresce on exposure, are easily soluble in water, and are attacked with difficulty by acids.

Ammoniacal Derivatives of Iridium.

625 Iridium forms ammoniacal derivatives corresponding to iridious chloride, $IrCl_2$, and iridic chloride, $IrCl_4$, which are analogous to the corresponding platinum compounds (p. 1147).

[1] Joly and Leidié, *Compt. Rend.* 1895, **120**, 1341.
[2] *Annalen*, 1861, **117**, 357.

It also forms an extended series [1] of compounds corresponding to the trichloride, $IrCl_3$, which are similar to the cobaltic, chromic and rhodic compounds, and are most probably strictly analogous to these in constitution (pp. 1067, 1093).

1. *Iridious Compounds.—Dichloro-diammine-iridium* (*Iridiosammonium Chloride*), $[Cl_2(NH_3)_2Ir]$, is obtained by heating a solution of iridious chloride with an excess of ammonium carbonate and neutralising the solution with dilute hydrochloric acid. It is a yellow granular body, insoluble in water. The corresponding hydroxide is not known, and of the other salts only the sulphato-compound, $[SO_4(NH_3)_2Ir]$, has been prepared. This is obtained by heating the chloride with sulphuric acid when an easily soluble orange-coloured crystalline powder is formed.

Tetrammine-iridium Dichloride (*Iridiodiammonium Chloride*), $[(NH_3)_4Ir]Cl_2$, is obtained by prolonged boiling of the preceding chloride with excess of ammonia. On cooling, a whitish precipitate separates, and this is decomposed by boiling water with evolution of ammonia. The hydroxide has not been prepared. The sulphate can be obtained from the chloride, and crystallises in rhombic prisms, which are easily soluble in hot water and deflagrate on heating.

2. *Iridic Compounds.—Dichloro-tetrammine-iridium Dinitrate* (*Iridiodiammonium Chloronitrate*), $[Cl_2(NH_3)_4Ir](NO_3)_2$, is formed when concentrated nitric acid is gradually added to dichlorodiammine-iridium. It dissolves in hot water and crystallises in lustrous laminæ. If an excess of hydrochloric acid be added to a solution of this compound, the chloride is precipitated, crystallising from boiling water in violet octahedra. Silver nitrate precipitates only the half of the chlorine which it contains. Sulphuric acid converts the nitrate into the corresponding sulphate, $[Cl_2(NH_3)_4Ir]SO_4$, which crystallises in fine greenish needles.

3. *Iridium Sesqui-compounds. — Hexammine-iridium trichloride*, $[(NH_3)_6Ir]Cl_3$, is prepared by heating the following compound with ammonia at 140° and crystallises in colourless prisms.

Chloro-pentammine-iridium dichloride (*Purpureo-iridium chloride*), $[Cl(NH_3)_5Ir]Cl_2$, is produced by the action of ammonia on ammonium chloriridite and forms yellowish-brown octahedral

[1] Palmaer, *Ber.* 1889, **22**, 15; 1890, **23**, 3810; 1891, **24**, 2090; *Zeit. anorg. Chem.* 1895, **10**, 320; 1896, **13**, 211.

crystals, but has also been obtained as a flesh-coloured crystalline powder. Silver nitrate only precipitates two-thirds of its chlorine.

A large number of other pentammine-iridium derivatives have been described, as well as aquo-pentammine, tetrammine, and triammine compounds.

Detection and Estimation of Iridium.

626 Sal-ammoniac produces, in a tolerably concentrated solution of iridium, a dark-red crystalline precipitate, and the dark colour, sometimes observed in the corresponding platinum precipitate indicates the presence of iridium in this metal. Iridium is also distinguished from platinum by the formation of a colourless solution of potassium chloriridate when caustic potash is added to the chloride of the metal, and on exposure to the air this colourless solution first becomes red-coloured, and afterwards blue. Sulphuretted hydrogen decolorises the solution of an iridic salt with separation of sulphur, whilst the brown sulphide, soluble in ammonium sulphide, is precipitated.

Iridium, like platinum, is always determined quantitatively as the metal.

The Atomic Weight of iridium was determined by Berzelius by igniting potassium chloriridate in hydrogen, the result of a single experiment being 196·5. Seubert,[1] in 1878, working with carefully purified material, obtained the number 191·57 by the analysis of the same salt, whilst the ignition of the ammonium salt gave the higher number 191·93. Joly,[2] in 1890, by the analysis of the potassium and ammonium chloriridites, obtained the number 191·78.

The most probable value may be taken as 191·7 (O = 15·88).

PLATINUM. Pt = 193·4.

627 This metal appears to have been first observed in the sixteenth century; for Scaliger, who died in 1558, in his work *Exercitationes Exotericæ de Subtilitate*, combated the views of Cardanus that all metals are fusible; for, he adds, in the mines

[1] *Ber.* 1878, **11**, 1770. [2] *Compt. Rend.* 1890, **110**, 1131.

of Mexico and Darian a metallic substance is found "quod nullo igni, nullis Hispanicis artibus, hactenus liquescere potuit." As platinum occurs in the above districts it appears very probable that this was the metal here referred to.

It was not, however, until two centuries later that platinum again attracted attention, and this time many chemists occupied themselves diligently with the subject. The first of these was Don Antonio de Ulloa, who took part in the French Expedition of 1735 which had for its object the measurement of an arc of the meridian on the equator. In 1748 he published his *Relacion Historica del Viage a la America Meridional*, in which he describes an unworkable metallic mineral which even makes gold ore useless if it occurs mixed with it in large quantities. William Watson[1] was the first to describe native platinum as a compact metal. He had obtained it nine years previously from Charles Wood, who had brought some samples of it from Carthagena in Granada to Jamaica, and thence to England. Watson termed it a semi-metal. It was afterwards more exactly examined by Scheffer, who describes it in the Memoirs of the Stockholm Academy in 1752 with the title "On White-gold, or the seventh Metal, termed in Spanish 'platina del Pinto,'" that is, small silver of Pinto, *platina* being the diminutive of *plata*, the Spanish for silver. The name of del Pinto was added because it was first found in the auriferous sand of that river. Scheffer describes the insolubility of platinum in nitric acid, and was acquainted with the facts that aqua regia dissolves it and that it is precipitated from the solution by mercury. He also states that it is infusible at the strongest heat of a furnace, but that it can be alloyed with other metals, and that it may be fused by the help of arsenic. He declares the new body to be a true metal, and, on account of its unalterability, believes it to be a noble one, and suggests that it may be used for the speculæ of telescopes. In 1754 Lewis[2] published a series of researches on platinum, and in 1757 the investigations of Marggraf were communicated to the Berlin Academy. Amongst the most important of his observations was that which has since proved of such service to analytical chemistry, that platinum solution produces with the salts of the alkalis an orange-yellow precipitate, with the exception of that of the mineral alkali soda, with which it produces none. Next came Macquer and Beaumé's researches on platinum, which were published in the Memoirs of

[1] *Phil. Trans.*, 1750.

[2] *Phil. Trans.* 1754, 638.

the Paris Academy for 1758. The most important new fact observed by these chemists was that platinum can be fused in the focus of a powerful burning-glass. Besides this, the paper in question contains the information that platinum had hitherto been so rare a substance, because the Spanish Government had forbidden its exportation, inasmuch as gold could be alloyed with a considerable quantity of the new metal without its colour being sensibly changed, thus giving rise to the possibility of fraud. Further investigations were made by Cronstedt in 1764 and by Bergman in 1777, the latter chemist explaining the nature of the changes which occur when a platinum solution is treated with the alkalis. Count von Sickingen, at that time the representative of the Palatinate at the Court of Paris, worked diligently on the subject of platinum, and was the first, in 1772, to prepare platinum foil and platinum wire, and to show that this metal dissolves in nitric acid when alloyed with silver. His experiments were communicated to the Academy in 1778, and in 1782 the same researches were described in a pamphlet which appeared in German with the title *Experiments on Platinum*. The whole of the preceding researches, as well as many of those carried on at a later time, were made with South American platinum.

In 1819 grains of a white metal were discovered in the auriferous sands of the Urals, but it was not till 1823 that platinum was detected in this substance. This discovery gave rise to the Scientific Expedition to the Urals undertaken by Humboldt, G. Rose and Ehrenberg, in 1829.

Platinum occurs only in the native state, but native platinum is very seldom pure, the purest specimens having been found in Brazil together with grains of palladium. The usual platinum "ore," as it is termed, contains all the metals of this group together with iron, copper, titanic iron ore, &c. It is sometimes, though seldom, found crystallised in cubes and octahedra, but more usually occurs in rounded or flattened grains, or sand having a metallic lustre, and occasionally in large rounded nuggets, both forms occurring in river sand or detritus. Some of the more important localities from which platinum is obtained are, Choco near Popayan in New Granada, the gold-washings of the Pinto in the province of Antioquia, and Minos Geraes in Brazil. In the Urals it is found in alluvial deposits at Nischnetagilsk and Goro-blagodat. Platinum likewise occurs in the Natoos Mountains in Borneo, which annually furnish some 600

to 800 pounds, and in Haiti, Peru, California, India, and Australia, especially in New South Wales, where it is now being worked. It is also found in small quantities in the sands of various rivers, occurring in the Rhine, and in streams in Wicklow, North Carolina, and Canada East. The largest mass which has yet been obtained is that in the Demidoff Cabinet in St. Petersburg, weighing 7·837 kilos. In the Urals platinum is found together with chrome-iron ore in serpentine, whilst in the Brazils it occurs with gold in syenite. Many common minerals such as dolomite, heavy spar, and fahl ore, &c., contain traces of platinum, and this explains the occurrence of the metal in the sands of so many rivers. It is also found in small quantities in most of the ores of lead and silver, and it is usually contained with palladium in small quantities in all silver.

The following table contains a series of analyses of various platinum ores by Deville and Debray:[1]

Locality.	Choco (S. America).	California.	Australia.	Urals.
Platinum . .	86·20	85·50	61·40	76·40
Gold	1·00	0·80	1·20	0·40
Iron	7·80	6·75	4·55	11·70
Iridium . . .	0·85	1·05	1·10	4·30
Rhodium . .	1·40	1·00	1·85	0·30
Palladium . .	0·50	0·60	1·80	1·40
Copper . . .	0·60	1·40	1·10	4·10
Osmiridium . .	0·95	1·10	26·00	0·50
Sand	0·95	2·95	1·20	1·40
	100·25	101·15	100·20	100·50

The body termed osmiridium is an alloy of osmium and iridium which is not attacked by aqua-regia, and the sand contains quartz, chrome-iron ore, hyacinth, spinelle, and titanic iron.

628 *The Metallurgy of Platinum.*—The infusibility of platinum, as well as its power of withstanding the action of many of the most powerful reagents, rendered it desirable that this metal

[1] *Ann. Chim. Phys.* 1859 [3], **56**, 449.

should be employed for the manufacture of vessels for chemical use. In 1784 Achard mentioned that the substance obtained by fusing arsenic and platinum together leaves, on ignition, a residue of malleable platinum, and in this way he prepared what was in all probability the first platinum crucible. This method was employed from the year 1787 in Paris, where Janetty was celebrated for his platinum work. Platinum vessels were, however, then and for some time afterwards so expensive and difficult to obtain, that in the year 1801 G. Rose and Karsten, for want of a platinum crucible, were unable to examine the statement of Guyton de Morveau and Desormes that potash consists of lime and hydrogen, and soda of magnesia and hydrogen.

In the year 1800 Richard Knight[1] published a method for preparing malleable platinum. This consisted in dissolving the crude platinum, precipitating the solution with sal-ammoniac, stamping the dried precipitate of the double chloride of platinum and ammonium into a conical mould made of fire-clay, and igniting the whole. In this way platinum is obtained as a coherent metallic mass, which can then be worked up. In 1822 a similar method was described by Barrual; but for many years before this, in fact from 1800 to 1809, a relative of a present member of the well-known firm of Messrs. Johnson, Matthey and Co., was employed in working on platinum, and had discovered (whether independently of Knight is uncertain) a method for consolidating the sponge, which was afterwards elaborated by Wollaston and described by him in the Bakerian Lecture[2] for 1828. This, although identical in the main features with Knight's process, is distinguished from it in several important particulars, and is the process by which platinum was manufactured up to the year 1859, when Deville's process came into use.[3] Wollaston in the first place pointed out the necessity of heating the double chloride very gently at a temperature just sufficient to expel the whole of the sal-ammoniac and to occasion the particles of platinum to cohere as little as possible, for on this depends the ultimate ductility of the product. The metallic powder thus obtained must be rubbed between the hands of the operator so fine as to pass through a fine lawn sieve. After having been well levigated, the uniform mud or pulp is pressed whilst cold into a brass

[1] *Tilloch's Phil. Mag.* 16, 1. [2] *Phil. Trans.* 1829, p. 1.
[3] *Ann. Chim. Phys.* 1859 [3], **56**, 484.

barrel and strongly compressed by a powerful lever. The cake of platinum can be easily removed, owing to the conical form of the barrel, and is now so hard that it can be handled without danger of breaking. It is then placed on a charcoal fire, and heated to redness to drive off moisture and to give it a greater degree of cohesion. After this it is heated in a wind furnace to the most intense heat that can be obtained. After ignition for about twenty minutes, the cake is removed from the furnace and placed upright on an anvil, and struck when hot on the top with a heavy hammer. The ingot of platinum thus obtained may be drawn into wire or submitted to any of the processes of which the most ductile metals are capable.

The easy method thus proposed for working up platinum has had a great influence on the progress of chemistry. The present generation of chemists can scarcely understand the difficulties which their predecessors had to contend with, unable, as they were, to use either platinum crucibles, basins, retorts, or platinum foil or wire. In his *Letters on Chemistry* Liebig says:

"Without platinum it would be impossible, in many cases, to make the analysis of a mineral. The mineral must be dissolved, and it must be first rendered soluble, or prepared for solution. Now, vessels of glass, of porcelain, and of all non-metallic substances are destroyed by the means we employ for that purpose. Crucibles of gold and silver would melt at high temperatures. But platinum is cheaper than gold, harder and more durable than silver, infusible at all temperatures of our furnaces, and is left intact by acids and alkali carbonates. Platinum unites all the valuable properties of gold and of porcelain, resisting the action of heat, and of almost all chemical agents. Without platinum the composition of most minerals would have yet remained unknown."

Platinum apparatus is also employed on a large scale and with great advantage in the chemical industries; thus, for example, in the manufacture of sulphuric acid, and in the parting of the noble metals. The first platinum apparatus for concentrating sulphuric acid, weighing 423 ounces, was made in London in 1809 by Messrs. Johnson, Matthey and Co., who since that time have furnished platinum vessels for all parts of the world.

The application of the oxyhydrogen blowpipe for fusing large masses of platinum proposed first by Hare[1] has exerted a

[1] *Phil. Mag.* 1847 [3], **31**, 356.

great influence on the progress of the platinum industry. Hare succeeded in fusing 971 grams of platinum, as well as large quantities of iridium and osmium. This method was improved upon by Deville and Debray,[1] whose investigations on the platinum metals have been of great service to the general progress of chemical industry. The means employed by these chemists for fusing platinum, and now employed on the large scale by most of the platinum manufacturers, consists in the use of two well-fitting lumps of quicklime. The upper one has a hole drilled through the middle for the introduction of the blowpipe, whilst a side opening permits the escape of the products of combustion and serves as an outlet for the molten metal. Instead of hydrogen common coal-gas is usually employed. This is allowed to enter through the tube H, Fig. 184, whilst the oxygen enters at O. The upper portion of the blowpipe consists of copper and the lower of platinum. Lime is used for the crucible, because it stands a high temperature well, and at the same time it absorbs the slags of the oxides of iron and silicon and other materials which are formed during the operation. The introduction of this process induced chemists to seek for a cheap method of preparing oxygen on the large scale (vol. i. pp. 220, 398), whilst by means of the oxy-hydrogen blowpipe Messrs. Johnson, Matthey and Co. have succeeded in effecting a most important improvement in the metallurgy of platinum, viz. that of soldering platinum by itself (autogenous soldering), instead, as was formerly the case, of soldering with gold.

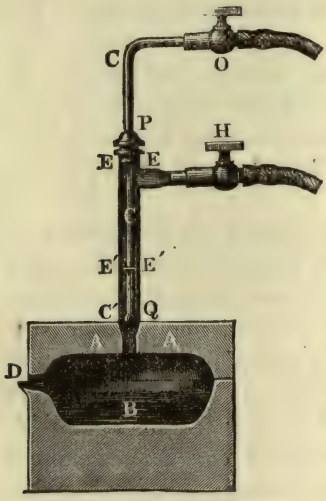


Fig. 184.

Deville and Debray also endeavoured to introduce a direct process for obtaining platinum from its ores in the dry way, and thus to replace Wollaston's tedious process of preparation. For this purpose they suggested two processes.[2] According to

[1] *Ann. Chim. Phys.* 1859 [3], **56**, 385.

[2] *Ann. Chim. Phys.* 1859 [3], **56**, 385; 1861, **61**, 5.

the first of these the ore, after having been mixed with lime, is simply fused. In this way an alloy of platinum with iridium and rhodium is obtained. This method is especially applicable to the fusion of old platinum vessels, inasmuch as all the impurities, such as sulphur, phosphorus, iron, gold, lead, &c., which occur in the scrap-platinum, are either volatilised or absorbed by the lime. The second method depends on the fact that lead can be alloyed with the platinum metals but not with osmiridium. The platinum ores always contain iron, and hence galena is employed instead of metallic lead, and glass and borax are added as fluxes. This operation is carried out in an ordinary melting crucible. The osmiridium which does not alloy with the lead is allowed to deposit by its higher specific gravity, and litharge gradually added until no further evolution of sulphur dioxide takes place. After cooling, the osmiridium, which remains at the bottom, is separated from the upper mass, the lead alloy cupelled, and the remaining platinum, containing a small quantity of iridium and rhodium, fused in a lime crucible with the oxyhydrogen blowpipe. These processes have, however, not met with much success in practice, inasmuch as there is no guarantee that the platinum thus prepared does not contain, in addition to the iridium and rhodium, which are harmless constituents, other admixtures, or that the metal thus obtained is homogeneous. Hence up to the present time Wollaston's process of preparation by the wet way is universally made use of. The following process for this purpose is adopted in the German works of Heräus in Hanau.[1] The raw ore is treated in glass retorts under a pressure of twelve inches of water with a mixture of 1 part of aqua-regia and 2 parts of water. The solution is evaporated to dryness, and the dried mass heated to 125°, at which temperature the palladium and rhodium salts are reduced to lower chlorides. The clear aqueous extract acidified by hydrochloric acid is then precipitated with sal-ammoniac, the pure double chloride of platinum and ammonium being thrown down, whilst the corresponding iridium salt is obtained on evaporating the mother-liquor. The solution remaining after precipitating the platinum salt is treated with scrap-iron, when the other metals are thrown down, and the precipitate, from which the excess of iron has been dissolved by hydrochloric acid, again treated with aqua-regia, and from this solution a new portion of platinum and iridium thrown down.

[1] Philipp, *Ber. Entw. Chem. Ind.* **1**, 999.

The mother-liquors, as well as the residue left on dissolving the ore in aqua-regia, contain the metals palladium, rhodium, ruthenium, osmium, and iridium. The spongy platinum obtained by igniting the double chloride of platinum and ammonium is then pressed, broken up in pieces, and fused with an excess of oxygen in a lime crucible. Most of the platinum which occurs in commerce is not pure, but contains, like Russian platinum coin, 2 per cent. of iridium. This alloy is especially valuable for the preparation of chemical vessels, inasmuch as it is less readily attacked by acids than pure platinum.

629 *Preparation of Pure Platinum.*—In order to prepare pure platinum various methods have been proposed. Deville and Debray[1] have prepared it on a large scale by the following process. The metal, which contains iridium and rhodium, is fused with from six to ten times its weight of lead, the mass after cooling treated with nitric acid, and the residue treated with dilute aqua-regia, when a crystalline alloy of iridium, ruthenium, and iron remains behind, whilst lead, platinum, and some rhodium go into solution. This latter is treated with sal-ammoniac, the double chloride $(NH_4)_2PtCl_6$ being thrown down in a finely-divided amorphous state and almost white, whilst the rhodium is kept in solution. The precipitate is washed with water containing hydrochloric acid, ignited, and the residual platinum fused in a lime crucible. When fused the supply of gas is suddenly stopped, so that the metal solidifies from the outside inwards, and in this way the formation of bubbles in the metal is avoided.

According to G. Matthey,[2] the preparation of pure platinum is a matter of great difficulty. His process is, to begin with, similar to that already described, but he evaporates down the aqua-regia solution, and then adds pure sulphuric acid to the residue in order to convert any lead which may remain in solution into the insoluble sulphate. The platinic chloride is then dissolved out by water and precipitated by a mixture of sal-ammoniac and common salt; this latter being added because the ammonium chloroplatinate is less soluble in a solution of common salt than in water. The liquid is then heated to 80° and allowed to stand for some days in order that the precipitate may become denser. This is then repeatedly washed with solution of sal-ammoniac, and at last with distilled water acidified

[1] *Compt. Rend.* 1875, **81**, 893. [2] *Proc. Roy. Soc.* 1879, **28**, 463.

with hydrochloric acid. The washed precipitate is then dried and mixed with potassium bisulphate, to which a small quantity of ammonium bisulphate has been added. The mixture is then heated to dark redness in a platinum basin. On boiling the mass with water, potassium sulphate and potassium rhodio-sulphate dissolve, leaving pure platinum behind.

The production of platinum from the Ural mines, which are now almost the only source of the metal, has been subject to great variations. In 1825, when the mines were first opened, only 361 pounds were produced. In 1827, the experiment of coining with platinum was tried at the St. Petersburg mint, pieces of 3, 6, and 12 roubles being produced. The coinage of platinum was, however, soon abandoned (in 1844), and the coins in circulation were withdrawn, owing to the very considerable variations which the price of the metal underwent from year to year and the impossibility therefore of fixing a permanent monetary value upon the coin. The total value coined amounted to 4,146,504 roubles, and the annual amount produced towards the close of the period in which the metal was coined reached 7,716·4 pounds. It afterwards declined, but has more recently again increased, owing to the large demand for the metal occasioned by the wide spread introduction of electric lighting, the metal being employed in the construction of incandescent lamps. In 1893 the production reached the amount of 11,196 pounds, the highest yet recorded. It is also largely used for the construction of chemical apparatus employed both in the laboratory and on the larger scale, for protecting other metals (platinising) and in the form of its salts for the preparation of photographic papers.

630 *Properties.*—Pure platinum has a tin-white colour, is soft like copper, has a specific gravity of 21·5, and is the most malleable of metals after gold and silver. Like iron, it can be readily welded at a white-heat, and an extremely fine wire can be melted in the flame of a Bunsen burner; but in large masses it is infusible even at the highest temperature of a blast-furnace, although a small piece of the metal may be melted in such a furnace.[1] It can, however, be fused in the oxyhydrogen flame. Deville estimates its melting-point at 2,000°. When large masses of the molten metal are quickly cooled, they exhibit the phenomenon of "spitting," so characteristic of silver. It readily volatilises in the electric arc.

[1] Meyer, *Ber.* 1896, **29**, 850.

Tubes made from fused and hammered platinum allow hydrogen to pass through them at a strong red-heat in larger quantity than is the case with caoutchouc membranes at the ordinary temperature. This property depends upon the fact that the red-hot metal has the power of absorbing hydrogen (Vol. i. p. 137), taking up 3·8 volumes of the gas, which it gives off on heating in a vacuum, the surface of the platinum becoming in this case covered with bubbles. The same phenomenon is noticed when platinum foil is employed as the negative pole in the electrolysis of water, the absorbed hydrogen being again given off when it is converted into the positive pole.

In January, 1817, Sir Humphry Davy communicated the fact to the Royal Society that mixtures of oxygen or air with hydrogen, carbon monoxide, ethylene, vapour of alcohol, vapour of ether, and other easily inflammable gases or vapours, are capable of bringing about the incandescence of a warmed platinum wire,[1] and that then these mixtures either combine slowly or in some cases quickly, and even with explosion. This now well-known phenomenon is thus described by Davy: "A temperature much below ignition only was necessary for producing the curious phenomenon, and the wire was repeatedly taken out and cooled in the atmosphere till it ceased to be visibly red, and yet when admitted again it instantly became red hot." In the following year Erman observed that it was only necessary to warm the platinum wire to 50° to enable it to bring about this combination.

In 1820 Edmund Davy showed that the black powder deposited when a platinum solution is precipitated by sulphuretted hydrogen, the precipitate dissolved in nitric acid, and the liquid thus obtained mixed with its own volume of alcohol, possesses the property, when moistened with spirits of wine, of becoming ignited in the air. Two years later Döbereiner observed that spongy platinum, obtained by the ignition of the double chloride of platinum and ammonium, exhibits the same phenomenon when gently warmed with alcohol. In 1823 the same chemist noticed that when hydrogen is allowed to pass over spongy platinum in presence of air, the hydrogen gas is ignited, and upon this was founded the well-known Döbereiner's Hydrogen Lamp.[2] Faraday afterwards showed that chemically clean platinum acts in a similar way. The circumstances under

[1] *Phil. Trans.* 1817, p. 77.

[2] *Schw. J.* **42**, 60. *Tilloch's Phil. Mag.* **65**, 150.

which platinum and certain other metals exhibit this action were investigated by Thénard and Dulong in a research published in the same year.

In order to exhibit this action Davy's glow-lamp is used (Fig. 185). It is fed with a mixture of alcohol and ether, or with methyl alcohol; this is ignited in order to heat the spiral of platinum wire to redness. The flame is then blown out, and the mixed vapours of alcohol and ether rising from the moist wick are oxidised, and thus the spiral is kept brightly incandescent. The same phenomenon can be observed if a spiral of platinum-wire be hung in a small test-glass (Fig. 186), on the bottom of which a little ether has been poured. Another mode of showing the same experiment is to heat a small piece of platinum foil in the flame of a Bunsen's lamp, and then quickly

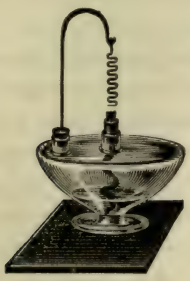


FIG. 185.

FIG. 186.

to extinguish the flame, allowing the gas to escape. The foil soon begins to glow, and if it be placed near the burner it becomes hot enough to re-ignite the gas; if further removed, the foil continues to glow, but the gas is not inflamed.

Spongy Platinum, first prepared by E. Davy, is very finely-divided metallic platinum, which possesses a very large surface compared with its mass, and is able to condense large quantities of oxygen. This substance is frequently employed as an oxidising agent, and may be readily prepared by gently heating the double chloride of platinum and ammonium. It then forms a porous mass, which, when heated strongly, becomes denser, and assumes a metallic lustre under the burnisher.

Platinum Black.—This form of platinum was also discovered by E. Davy, who, however, misled by certain accidental impurities, considered it to be a platinous nitrite. It is to Liebig[1]

[1] *Pogg. Ann.* 1829, **17**, 102.

that we owe the discovery of this error, and also a description of a good method for the preparation of the substance. This consists in warming a solution of platinum dichloride in potash with alcohol. Thus obtained it is a soft black dull powder, which soils any surface on which it is rubbed. When thoroughly freed from alcohol by boiling with water, and dried in a vacuum over sulphuric acid, it absorbs oxygen from the air so rapidly that the mass becomes red-hot. Platinum black is also obtained by dissolving alloys of platinum with other metals, such as copper and zinc, in nitric acid, when the platinum remains in the form of a black powder. This latter preparation, heated in open vessels to a temperature considerably below redness, deflagrates with a hissing noise, sometimes detonating like gunpowder. Platinum black is also obtained when platinum is precipitated by other metals from a dilute solution, or when such solution is treated with reducing agents. Thus, for instance, if a solution of platinic chloride be allowed to drop into a boiling mixture of three volumes of glycerine and two of caustic potash of specific gravity 1·08, the black obtained possesses extremely active properties,[1] as does that prepared by the reduction of platinic chloride by means of formaldehyde.[2] According to Liebig, platinum-black absorbs more than 800 times its volume of oxygen, whereas the black prepared by Mond, Ramsay and Shields was found to contain 100 volumes of oxygen. When brought into hydrogen 310 volumes were taken up, 200 of which united with the oxygen present to form water, whilst the remaining 110 were absorbed.[3] After frequent ignition in a mixture of combustible gas and air, the black becomes denser, approaching spongy platinum in its properties. Platinum-black is frequently used in organic chemistry as an oxidising agent, and it has been successfully applied in place of oxide of copper in organic analysis.[4]

Platinum is not oxidised at any temperature by oxygen, water, sulphuric acid, or nitric acid. It is not attacked by sulphur alone, although action takes place if alkalis are present. These latter, as well as nitre, oxidise the metal, and for this reason fusion with alkalis or nitre ought not to be performed in platinum vessels. Alkali cyanides should not be fused in contact

[1] Zdrawkowitch, *Bull. Soc. Chim.* 1876 [2], **25**, 198.
[2] Loew, *Ber.* 1890, **23**, 289.
[3] *Proc. Roy. Soc.* 1895, **58**, 242.
[4] Kopfer, *Journ. Chem. Soc.* 1877, i. 228.

with platinum, as these likewise attack the metal. It is also inadvisable to expose platinum vessels to direct contact with burning charcoal, as the silicon reduced from the charcoal-ash unites with the metal, making it brittle and liable to crack. Especially to be avoided is contact at a high temperature with compounds of the easily reducible metals, as these readily form fusible alloys with the platinum. Phosphorus and arsenic also combine with platinum when heated with it. When platinum vessels are heated over a smoky flame, or in one in which the supply of air is insufficient to bring about complete combustion, the surface of the platinum becomes disintegrated, probably owing to the successive formation and decomposition of compounds of the metal with carbon from the flame.

The best method of cleaning a platinum crucible is to fuse in it some potassium bisulphate (Gmelin), and in order to test whether a new platinum crucible is of proper quality it is first boiled with hydrochloric acid, and afterwards with pure nitric acid. If none of the metal is dissolved, the platinum is good.

COMPOUNDS OF PLATINUM.

Platinum and Oxygen.

631 Three oxides of this metal are known :

Platinum monoxide, or platinous oxide, PtO, giving rise to the platinous salts, platinum dioxide, or platinic oxide, PtO_2, giving rise to the platinic salts, and platino-platinic oxide, Pt_3O_4.[1]

Platinum Monoxide, PtO, is obtained as a grey powder by the careful ignition of the hydroxide, or as a violet powder by igniting the compound of platinic oxide and lime (see p. 1138), and treating the residue with nitric acid. When strongly heated it passes into the metal, deflagrating when heated with charcoal. It is reduced to platinum black when heated with aqueous formic acid, CH_2O_2, with violent evolution of carbon dioxide.

Platinous Hydroxide, $Pt(OH)_2$, is obtained by decomposing the dichloride with hot caustic potash. The whole of the chlorine cannot, however, be removed in this way, and if caustic soda be employed, a product is obtained from which the soda cannot be completely washed out (Liebig). It is prepared in the

[1] Jörgensen, *J. pr. Chem.* 1877 [2], **16**, 344.

pure state by mixing one part of potassium chloroplatinite, K_2PtCl_4, with twelve parts of water, adding the exact quantity of dilute caustic soda necessary for decomposition, and heating the mixture to boiling until the alkaline solution has become neutral. It dissolves in hydrochloric, hydrobromic, and sulphurous acids, but not in other oxyacids. Boiling caustic potash decomposes it into metal and the dioxide. It acts as a weak base, of which the haloid salts as well as a few double salts of the oxyacids have been prepared.

Platinum Dioxide, PtO_2, is obtained as a black powder by gently heating the corresponding hydroxide.

Platinum Tetrahydroxide or *Platinic Hydroxide*, $Pt(OH)_4$, is prepared by boiling the solution of platinic chloride with caustic potash, when a basic double salt is precipitated, and this is heated with acetic acid in order to dissolve out the alkali. In this way it is obtained as an almost white precipitate, which on drying becomes yellow, and then possesses the above composition. It dissolves readily in caustic soda and in dilute acids. At 100° it loses its water and assumes an amber colour. Platinic hydroxide acts both as a weak base and as an acid-forming oxide. With bases it yields salts termed *platinates*,[1] of which, however, only the sodium salt has been obtained in the pure state. This possesses the composition $Na_2O.3PtO_2+6H_2O$, and is a reddish-yellow, partially crystallised powder. It is obtained when a clear aqueous mixture of chloroplatinic acid and sodium carbonate is exposed to sunshine, or when the mixture is heated for some time to 100°. The aqueous solution of the two salts may also be evaporated to dryness, and the residue boiled out with water, when a denser precipitate of the same compound is obtained, having an ochre-yellow colour. When an excess of lime-water is added to a solution of platinic chloride, and this exposed to sunlight, a white or yellowish pulverulent precipitate falls down, to which the name of calcium platinate has been given,[2] its composition corresponding approximately to the formula $CaPt_2O_5+CaCl_2+7H_2O$. If the hydroxide be boiled with a solution of a polymolybdate, or a polytungstate, salts of the following acids are formed:

Platinmolybdic acid, $H_8PtMo_{10}O_{36}$.
Platintungstic acid, $H_8PtW_{10}O_{36}$.

[1] See Rousseau, *Compt. Rend.* 1889, **109**, 144.
[2] Herschel, *Phil. Mag.* 1832 (2), **1**, 58.

These acids and their salts have a yellow or greenish colour, and are crystalline.[1]

Platino-platinic Oxide, Pt_3O_4, is obtained as a black insoluble powder by heating sodium chloroplatinate with sodium carbonate and extracting with water.

Platinum and the Halogens.

632 *Platinous Fluoride*, PtF_2, is formed when platinum wire is heated to dull redness in a current of fluorine. It is thus obtained as a deep red coloured mass, which is very hygroscopic, and is decomposed by water slowly in the cold, more rapidly on heating. When the anhydrous substance is heated, it yields fluorine and leaves crystalline platinum.[2]

Phosphorus pentafluoride acts on spongy platinum at a red-heat to form volatile crystals of the formula PF_3PtF_2.[3]

Platinous Chloride or *Platinum Dichloride*, $PtCl_2$, is formed when chloroplatinic acid, H_2PtCl_6, obtained by dissolving the metal in aqua-regia and crystallising, is heated to 300°, or when spongy-platinum is heated in a current of dry chlorine to between 240° and 250°.[4] It is a greenish-grey powder, having a specific gravity of 5·87, which is not readily moistened with water, and is insoluble in this liquid. It decomposes on heating into platinum and chlorine.[5]

Platinum dichloride unites with phosphorus trichloride to form the compound $PtCl_2PCl_3$, which is obtained by heating spongy-platinum with pentachloride of phosphorus to 250°. The product is easily soluble in benzene or chloroform, and crystallises from these liquids in fine brown needles. When dissolved in water and the solution evaporated in a vacuum, orange-yellow deliquescent prisms of *chloroplatinophosphorous acid*, $PtCl_2P(OH)_3$, are obtained. This has an acid metallic taste, and yields a white precipitate with silver nitrate and a yellow one with acetate of lead. Corresponding salts of the alkali metals have not been prepared, as hydroxides and carbonates decompose the acid.

[1] Gibbs, *Ber.* 1877, **10**, 1384.
[2] Moissan, *Compt. Rend.* 1889, **109**, 807.
[3] Moissan, *Bull. Soc. Chim.* 1891 (3), **5**, 454.
[4] Schützenberger, *Ann. Chim. Phys.* 1870 [4], **21**, 351.
[5] See Shenstone, *Journ. Chem. Soc.* 1892, i. 450.

The foregoing compound readily takes up another molecule of phosphorus trichloride, forming $PtCl_2(PCl_3)_2$, which may likewise be crystallised from chloroform or benzene in large deliquescent prisms, which melt at 160°, and when strongly heated give off phosphorus trichloride. If these are allowed to remain in contact with water at a winter temperature, or if their solution be evaporated at a low temperature in a vacuum, very deliquescent yellow needles are obtained of *chloroplatinodiphosphorous acid*, $PtCl_2 2P(OH)_3$, and this readily undergoes decomposition at 12°, with evolution of hydrochloric acid, into the compound $PtClOP_2(OH)_5$. This latter forms white crystals, is less deliquescent than the former compounds, and when heated to 150° is converted into a light-yellow non-deliquescent powder, having the composition $PtClO_2P_2(OH)_3$. The solution of this compound, like the preceding, is precipitated by nitrate of silver.[1]

Carbonyl Chloroplatinites.—When platinous chloride is heated to a temperature of 250° in a current of carbon monoxide the following compounds are formed:

$PtCl_2.2COCl_2$.
$PtCl_2.CO$,
$PtCl_2.(CO)_2$,
$(PtCl_2)_2(CO)_3$.

The last named is produced in largest quantity and is obtained in the pure state by boiling the crude product with carbon tetrachloride. In this way fine orange-yellow needles melting at 130° are obtained, and these when heated to from 250° to 260° in dry carbon dioxide yield the compound $PtCl_2.CO$ in fine needles which melt at 194° and may be partially sublimed in a current of dry carbon dioxide at 240°, and at 300° decompose into carbonyl chloride, $COCl_2$, and platinum. When this compound, or the crude product, is heated to 150° in carbon monoxide, the compound, $PtCl_2.2CO$, sublimes in white needles which melt at 142°.[2] All these compounds are decomposed by water with separation of the metal and formation of carbon dioxide and hydrochloric acid.

633 *Chloroplatinites* or *Platinochlorides.*—The solution of platinous chloride in hydrochloric acid may be regarded as *chloroplatinous acid*, H_2PtCl_4. The potassium salt is the usual

[1] Schützenberger, *Bull. Soc. Chim.* 1872 [2], **17**, 482; **18**, 153.

[2] Schützenberger, *Ann. Chim. Phys.* 1868 [4], **15**, 100, and 1870, **21**, 325; Pullinger, *Journ. Chem. Soc.* 1891, i. 598.

starting point for the preparation of this compound and its salts.[1]

Potassium Chloroplatinite, K_2PtCl_4.—This salt, which was first prepared by Magnus,[2] is easily obtained by adding moist cuprous chloride to a thick paste of potassium chloroplatinate, K_2PtCl_6, and water, in such quantity that a small portion remains unreduced. On cooling the filtered liquid, the greater portion of the platinous salt separates out, the mother-liquor yielding a second crop on concentration, whilst the remainder of the salt is precipitated from the last portion of the liquor with alcohol. These various crops are then washed with alcohol and the pure salt obtained by recrystallisation from hot water. It forms soft rose-coloured crystalline fibres. When the requisite quantity of chloroplatinic acid is added to the hot saturated solution of this salt a precipitate of potassium chloroplatinate is separated and an almost pure solution of chloroplatinous acid, H_2PtCl_4, is obtained. The same acid is produced by treating the barium salt with dilute sulphuric acid. On evaporation in a vacuum over sulphuric acid or caustic potash a solid compound separates out which dries up with loss of hydrochloric acid, forming a brown amorphous mass of $H_2Pt(OH)Cl_3 + H_2O$.[3] By dissolving oxides, hydroxides, carbonates or chlorides in the acid a series of compounds are obtained which have been fully described by Nilson.

Ammonium Chloroplatinite, $(NH_4)_2PtCl_4$.—This salt was first described by Vauquelin and afterwards by Peyronne. It crystallises from solution in hot water in large red four-sided prisms or in thin tablets.

Most of the other chloroplatinites crystallise with water in fine red or brown crystals which are often deliquescent; some such as the silver salt, Ag_2PtCl_4, and the lead salt, $PbPtCl_4$, are flesh-coloured precipitates.

Platinic Chloride or *Platinum Tetrachloride*, $PtCl_4$.—When metallic platinum is heated in a current of chlorine it is attacked, and this compound is slowly formed. The action diminishes when the temperature is raised, as the tetrachloride decomposes into metal and chlorine at 500°. If, however, the temperature be raised to 1,300°, the formation of tetrachloride recommences; and if an excess of chlorine be employed and

[1] J. Thomsen, *J. pr. Chem.* 1877 [2], **15**, 294.
[2] *Pogg. Ann.* 1828, **14**, 241.
[3] Nilson, *J. pr. Chem.* 1877 [2], **15**, 260.

the temperature raised to 1,700°, the action becomes rapid and a yellow sublimate of tetrachloride is deposited.[1] The same reaction occurs if a spiral platinum-wire be heated by an electric current nearly to its melting-point in a stream of chlorine. At the thick end of the wire crystals of metallic platinum are deposited. These are not formed owing to any volatility of the metal, but are produced by the alternate production and decomposition of the tetrachloride.[2]

The anhydrous chloride is also formed when crystallised chloroplatinic acid is dried over sulphuric acid and then heated to 369° in a current of chlorine,[3] or at 165° in a current of hydrochloric acid.[4]

By mixing solutions of aqueous chloroplatinic acid and silver nitrate in the proportion of one molecule of the former to two of silver nitrate, a precipitate of silver chloroplatinate is thrown down, which is decomposed by hot water into silver chloride and platinic chloride. The yellowish-red solution yields on evaporation over sulphuric acid fine large red apparently monosymmetric crystals of the composition $PtCl_4 + 5H_2O$. They are not deliquescent, and their concentrated solution is only slowly precipitated with sal-ammoniac on standing.[5] With ammonia the crystals are converted into the acid $PtCl(OH)_3$.[6]

Hydrates containing one, four, and seven molecules of water have also been prepared.

Chloroplatinic Acid, H_2PtCl_6.—This compound, which is often erroneously called platinum chloride, is obtained by dissolving the metal in aqua-regia and evaporating with hydrochloric acid until all nitric acid is removed. It crystallises in brownish-red very deliquescent prisms having the composition $H_2PtCl_6 + 6H_2O$. If the solution be repeatedly evaporated with aqua-regia nitrosoplatinic chloride, $(NO)_2PtCl_6$, is formed. This crystallises in small orange-coloured cubes and is very deliquescent, dissolving in water with evolution of nitric oxide, the nitrogen trioxide which is at first evolved being decomposed by water.

[1] Troost and Hautefeuille, *Compt. Rend.* 1887, **84**, 946 ; Langer and Meyer, *Pyrochem. Untersuch*, p. 57.

[2] Hodgkinson and Lowndes, *Nature*, May 3, 1888.

[3] Pigeon, *Compt. Rend.* 1890, **110**, 77 ; 1891, **112**, 1218 ; *Ann. Chim. Phys.* 1894 (7), **2**, 433.

[4] Pullinger, *Journ. Chem. Soc.* 1892, i. 422.

[5] Norton, *Journ. Chem. Soc.* 1872, 680.

[6] Jörgensen, *J. pr. Chem.* 1877 (2), **16**, 345.

The hydrogen in chloroplatinic acid can be readily replaced by metals, and thus a series of crystalline salts termed the *chloroplatinates* or the *platinichlorides* are obtained, of which the most important are those of the alkali metals, their widely differing solubilities rendering them very valuable in analytical chemistry.

Potassium Chloroplatinate or *Potassium Platinichloride* K_2PtCl_6, is thrown down, on the addition of potash or a potassium salt to the acid, in the form of a yellow crystalline precipitate which is deposited from solution in hot water in the form of small reddish-yellow octohedra having a specific gravity of 3·586. One hundred parts of water dissolve, according to Bunsen and Kirchhoff, as follows:

At 0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	
0·70	0·90	1·12	1·41	1·76	2·17	2·61	3·19	3·79	4·45	5·18	parts.

It is insoluble in a saturated solution of potassium chloride as well as in alcohol. It dissolves in caustic potash and is precipitated from the solution on the addition of acids.

Sodium Chloroplatinate, $Na_2PtCl_6+6H_2O$, is obtained by evaporating the acid with common salt, when light-red asymmetric prisms or tables are deposited which have a specific gravity of 2·499. These become anhydrous at 100°, falling to a yellowish-red powder, which is easily soluble in water and alcohol.

Lithium Chloroplatinate, $Li_2PtCl_6+6H_2O$, crystallises in large orange-yellow plates which effloresce in the air and are easily soluble in water and in a mixture of alcohol and ether, but not in pure ether.

Rubidium Chloroplatinate, Rb_2PtCl_6, closely resembles the potassium salt but is still more insoluble, 100 parts of water dissolving according to Bunsen the following amounts:

20°	40°	60°	80°	100°	
0·141	0·166	0·258	0·417	0·634	parts.

Caesium Chloroplatinate, $CsPtCl_6$, is the least soluble of the chloroplatinates of the alkali metals, 100 parts of water dissolving:

20°	40°	60°	80°	100°	
0·070	0·142	0·213	0·291	0·377	parts.

It forms, like the rubidium salt, microscopic glistening honey-yellow transparent octahedra.

Ammonium Chloroplatinate, $(NH_4)_2PtCl_6$, is obtained by precipitating the acid with an ammonium salt, as a lemon-yellow crystalline powder, which crystallises from hot water in orange-yellow octahedra; these have a specific gravity of 3·0, and are indistinguishable in appearance from the potassium salt. One hundred parts of water dissolve at the ordinary temperature about 0·666, and at 100° 1·25 parts of the salt. It is not soluble either in alcohol or ether, and scarcely soluble in a solution of sal-ammoniac. On heating it decomposes without fusion, leaving pure platinum-sponge behind.

Platinous Bromide, $PtBr_2$, is obtained by heating bromoplatinic acid to 280°, and forms a brown mass which dissolves with a brownish-red colour. If boiling saturated solutions of potassium chloroplatinite and potassium bromide are mixed double decomposition occurs and the potassium chloride may be separated from the *potassium bromoplatinite*, K_2PtBr_4, by crystallisation. The latter forms large nearly black pyramids or brownish-red needles (Thomsen). Like the chloride it unites with carbon monoxide, forming a compound $PtBr_2.CO$. (Pullinger.)

Platinic Bromide, $PtBr_4$.—Bromine acts upon platinum at different temperatures in the same way as chlorine. The tetrabromide is best obtained by heating spongy platinum with bromine and hydrobromic acid to 180°, evaporating the solution and drying the residue at 180°. It is a brownish-black deliquescent powder, nearly insoluble in water, but readily soluble in alcohol and ether, yielding a brown solution.[1] When platinum is dissolved in a mixture of nitric and hydrobromic acids, and the concentrated solution allowed to evaporate over quicklime, dark-red monosymmetric prisms of *bromoplatinic acid*, $H_2PtBr_6 + 9H_2O$, are deposited, which are very deliquescent. This compound gives rise to a series of bromoplatinates corresponding to the chloroplatinates, most of which possess a red colour.

Platinous Iodide, PtI_2, is formed by warming the chloride with a solution of potassium iodide. It is a black powder closely resembling lamp-black in appearance.

Platinic Iodide, PtI_4, is a black or brownish-black amorphous powder obtained by the action of hydriodic acid on a soluble chloroplatinate. *Iodoplatinic acid*, $H_2PtI_6 + 9H_2O$, easily decomposes into water, hydriodic acid, and platinic iodide. The

[1] V. Meyer and Züblin, *Ber.* 1880, **13**, 404; Halberstadt, *Ber.* 1884, **17**, 2962.

iodoplatinates are brown and possess a metallic lustre; they are soluble in water and are very unstable, giving off iodine at a temperature below 100°.

Platinum and the Elements of the Sulphur Group.

634 *Platinum Monosulphide*, PtS, is formed when platinum sponge is heated with sulphur in a vacuous glass tube, or when platinous chloride is fused with sodium carbonate and sulphur, and the mass extracted with water. It forms a green powder or a mass of glistening needles.[1] When heated in the air it decomposes, leaving a residue of platinum, and when ignited in hydrogen it yields sulphuretted hydrogen and spongy platinum.

Platinum Disulphide, PtS_2, is formed as a steel-grey powder by heating ammonium chloroplatinate with sulphur to a dark-red heat. When sulphuretted hydrogen is passed through a solution of a platinic salt a black precipitate of sulphide is first formed, but this by further action of the gas becomes light-brown, from formation of hydrogen platinum sulphide, a compound which on exposure to the air again gives up sulphuretted hydrogen.

Platinum disulphide combines with basic sulphides and therefore dissolves in the sulphides of the alkali-metals.

Potassium Platinothioplatinate, $K_2Pt_4S_6 = K_2S + 3PtS + PtS_2$, is obtained by fusing together platinum sponge, potash, and sulphur, and lixiviating the mass with water. It then separates in the form of hard six-sided tables, which on heating in the air burn like tinder. Dilute sulphuric acid converts it into $H_2Pt_4S_6$, and this on exposure to air oxidises to *platinum sesquisulphide*, Pt_2S_3, forming a steel-grey crystalline powder.

Di-sodium Platinothioplatinate, $Na_4Pt_3S_6 = 2Na_2S + 2PtS + PtS_2$, is obtained in a similar way to the preceding compound, and forms pale copper-red thin crystalline needles which are converted in contact with hydrochloric acid, without alteration of form, into a reddish-brown compound, $H_4Pt_3S_6$, which oxidises extremely quickly in the air with formation of the sesquisulphide.[2]

Potassium Platinosulphite, $K_6Pt(SO_3)_4 + 2H_2O$.—A solution

[1] Debray and Deville, *Compt. Rend.* 1879, **89**, 587.
[2] Schneider, *Pogg. Ann.* 1866, **138**, 604.

of potassium chloroplatinite becomes decolorised when warmed with acid potassium sulphite, the above salt separating out from the solution in yellowish or colourless needles. Sodium salts precipitate from this solution *Sodium platinosulphite*, $Na_6Pt(SO_3)_4 + 7H_2O$, in microscopic needles. *Ammonium Platinosulphite*, $(NH_4)_6Pt(SO_3)_4$, is obtained by similar means.

These compounds must be regarded as salts of complex acids, since they do not show the ordinary reactions for either platinum or sulphurous acid.

Platinic Sulphate, $Pt(SO_4)_2$, is obtained as a brown mass by acting on the hydroxide or chloride with sulphuric acid and evaporating the solution.

Platinum Selenide.—Spongy platinum unites with selenium with incandescence when these substances are heated together, with formation of a grey infusible powder, which when heated before the blowpipe, loses the whole of its selenium.

Platinum and the Elements of the Nitrogen Group.

635 *The Platinonitrites* or *Nitrito-platinites.*—These compounds are probably analogous in composition to the ammoniacal derivatives corresponding to the platinous salts (p. 1147), and behave not as double salts, but as salts of a complex acid, for they do not show the usual reactions either of platinum salts or nitrites. They were first described by Lang,[1] and afterwards investigated more completely by Nilson.[2]

Potassium Platinonitrite, $K_2Pt(NO_2)_4$, is obtained when solutions of potassium nitrite and potassium chloroplatinate are warmed together. It is deposited in the form of small glistening six-sided prisms, which dissolve in 27 parts of water at 15°, and at a higher temperature in a smaller quantity. Alkalis do not precipitate platinum oxide, and sulphuretted hydrogen does not precipitate sulphide of platinum from its solution. When the solution is allowed to evaporate spontaneously, rhombic tables having the composition $K_2Pt(NO_2)_4 + 2H_2O$ separate out, which effloresce readily. It readily combines with a molecule of chlorine or bromine.[3]

Silver Platinonitrite, $Ag_2Pt(NO_2)_4$, is obtained when solutions

[1] *J. pr. Chem.* 1861, **83**, 415. [2] *Ber.* 1876, **9**, 1722; 1877, **10**, 934.
[3] Blomstrand, *J. pr. Chem.* 1871 [2], **3**, 207; Vèzes, *Compt. Rend.* 1891, **112**, 616; **113**, 696.

of the potassium salt and silver nitrate are mixed. On recrystallising the precipitated salt from hot water, large yellow glistening monosymmetric prisms are obtained, which on heating decompose with incandescence and detonation.

Barium Platinonitrite, $BaPt(NO_2)_4 + 3H_2O$, is obtained by decomposing the silver salt with chloride of barium. It crystallises from solution in hot water in colourless octahedra. If this salt be decomposed by dilute sulphuric acid, and the solution evaporated in a vacuum over caustic potash, microscopic crystals having the colour of chromium trioxide separate out; these possess, according to Lang, the composition $H_2Pt(NO_2)_4$. Nilson was unable to obtain this compound. The solution yielded, on evaporation, a gummy mass and a green glistening residue, having the composition $H_4Pt_2O(NO_2)_8 + 2H_2O$. On neutralisation with potash and evaporation, this yielded the potassium salt $K_4Pt_3O(NO_2)_8 + 2H_2O$ in oblique four-sided glistening light-yellow tablets.

Fulminating Platinum.—E. v. Meyer has examined a series of explosive compounds obtained by acting upon ammonium chloroplatinate by potash, the existence of some of which was pointed out long ago by Proust and Döbereiner. Their constitution is as yet unknown; the yellow precipitate obtained on heating ammonium chloroplatinate with potash has the composition $PtClNH_6O_2$.[1]

Ammoniacal Platinum Compounds.

636 Like the salts of cobalt and most of the metals of this group, the various platinum salts are capable of forming peculiar basic compounds with ammonia, the constitution of which is yet but imperfectly understood. The first of these compounds was obtained in 1828 by Magnus.[2] By the action of ammonia on platinous chloride he obtained a green insoluble salt having the empirical composition $PtCl_2(NH_3)_2$, which is well known as Magnus's green salt. Gros[3] then obtained a series of light-yellow or colourless salts by the action of nitric acid upon the green salt of Magnus. Reiset[4] and Peyronne[5] independently found that by

[1] *J. pr. Chem.* 1878 (2), **18**, 305.
[2] *Pogg. Ann.* 1828, **14**, 204.
[3] *Ann. Chim. Phys.* (2), **69**, 204.
[4] *Ann. Chim. Phys.* 1844 (3), **11**, 417; *Compt. Rend.* 1840, **10**, 870; 1844, **18**, 1103.
[5] *Ann. Chim. Phys.* 1844 (3), **12**, 193; 1846 (3), **16**, 462.

the action of ammonia on Magnus's green salt, or on platinous chloride, two other series of compounds could be obtained. These were distinguished as the chlorides of Reiset's first and second bases. Peyronne showed that Magnus's salt is a chloroplatinate of the second base. Further investigations of these compounds, and theoretical speculations concerning their constitution, have been made by various other chemists.[1]

The constitution of these compounds is probably similar to that of the cobalt bases, and has been similarly interpreted, according to each of the two views already discussed (p. 1069). Unlike the cobalt compounds, however, these derivatives exist in two series, in which the platinum is divalent and tetravalent respectively.

In the platinous series, the metal is capable of combining with only 4 molecules or radicals to form the characteristic complex group, and the maximum number of external acid radicals is 2, since the platinum is divalent.

In the platinic series, on the other hand, the metal, like cobalt, is capable of forming a complex group with 6 molecules or radicals, but, platinum being in these salts tetravalent, the maximum number of external radicals is 4, instead of 3 as in the derivatives of trivalent cobalt.

The classification is based on the same principles as that indicated for the compounds of cobalt, namely, the number of ammonia molecules contained in the complex group, and the constitutions assigned to the various compounds are in accordance with the electrical conductivity of the compounds in aqueous solution.

It is characteristic of the platinum series that the free hydroxides from which the salts are derived are in many cases stable substances, whereas this is rarely the case in the cobalt series.

[1] Raewsky, *Ann. Chim. Phys.* 1844 (3), **12**, 278; Gerhardt, *Compt. Rend.* 1850, **31**, 244; Buckton, *Annalen*, 1852, **84**, 220; Thomsen, *Ber.* 1870, **3**, 42; Odling, *Ber.* 1870, **3**, 42; Blomstrand, *Ber.* 1871, **4**, 673; Cleve, *Bull. Soc. Chim.* 1867 (2), **7**, 12; 1871, **15**, 161; **16**, 203; 1872, **17**, 289; Cossa, *Journ. Chem. Soc.* 1887, ii. 642; 1896, **2**, ii. 251; *Ber.* 1890, **23**, 2503; *Zeit. anorg. Chem.* 1891, **1**, 65; Werner, *Zeit. anorg. Chem.* 1893, **3**, 267; 1895, **8**, 153; 1896, **12**, 46, &c., &c.

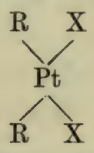
Platinous Compounds.

The isomerism of these compounds may be due to two causes:—

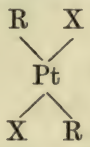
1. The position of the radical inside or outside the complex group.

2. The arrangement of the four members of the complex group around the platinum atom.

All the cases of the second kind hitherto observed are satisfactorily accounted for by supposing that these molecules or radicals are arranged in one plane symmetrically about the platinum atom. Isomerides are then only possible when the complex group has the general formula $Pt_2R_2X_2$, the possible cases being represented by the two following diagrams:—



Asymmetric.
(Platosemidiammine.)



Symmetric.
(Platosammine.)

The following are the chief series of these derivatives which have been described, R and M being monovalent acid and basic radicals.

1. Tetrammine-platinous compounds, $[(NH_3)_4Pt]R_2$.
   (Plato-diammine.)
2. Triammine-platinous compounds, $[R(NH_3)_3Pt]R$.
   (Plato-monodiammine.)
3. Diammine-platinous compounds, $[R_2(NH_3)_2Pt]$.
   (Platosammine and platosemidiammine.)
4. Monammine-platinous compounds, $[R_3(NH_3)Pt]M$.
   (Platosemiammine.)

Platinic Compounds.

The cases of geometrical isomerism which occur among these derivatives are explained in a similar manner to those of the cobaltammines.

1. Hexammine-platinic compounds, $[(NH_3)_6Pt]R_4$.
   (Drechsel's base.)

2. Pentammine-platinic compounds, Unknown.
3. Tetrammine-platinic compounds, $[R_2(NH_3)_4Pt]R_2$. (Platin-diammine.)
4. Triammine-platinic compounds, $[R_3(NH_3)_3Pt]R$. (Platinmonodiammine.)
5. Diammine-platinic compounds, $[R_4(NH_3)_2Pt]$. (Platinammine and platinsemidiammine.)
6. Monammine-platinic compounds, $[R_5(NH_3)Pt]M$. (Platinisemiammine.)

Just as in the cobalt series these complex radicals are capable of acting as mono-, di-, and tri-valent radicals, and thus form a very large number of derivatives.

The original green salt of Magnus, $[(NH_3)_4Pt]PtCl_4$, which was the first of the ammoniacal derivatives of platinum to be discovered, is, for example, nothing else than the compound of tetrammine-platinous chloride, $[(NH_3)_4Pt]Cl_2$, with platinous chloride, $PtCl_2$, just as potassium chloroplatinite, K_2PtCl_4, is the double compound of platinous chloride, $PtCl_2$, and potassium chloride, KCl.

Magnus's Green Salt, which is the starting-point for the preparation of these derivatives, is made by the action of ammonia on platinous chloride, and when boiled with ammonia passes into *tetrammine-platinous chloride*, $[(NH_3)_4Pt]Cl_2$.

The tetrammine salts lose ammonia when heated, thus yielding the symmetrical diammine compounds (platosammine salts), whilst the isomeric asymmetrical compounds (platosemidiammine salts) are formed by the moderate action of ammonia on the platinous salts. The platinic salts are formed by the oxidation of the corresponding platinous derivatives.

In addition to the classes of compounds already mentioned, several others have been described, the members of which contain more than one atom of platinum. Very little is known of these latter compounds, for a detailed description of them reference must be made to the original papers.

Phosphide and Arsenide of Platinum.—These two elements fuse together readily. If finely divided platinum be heated in vapour of phosphorus it burns with evolution of light to form *platinum diphosphide*, PtP_2, which is a bright metallic lustrous mass, not attacked by hydrochloric acid, but easily dissolved by ammonia (Schrötter).

Spongy platinum and arsenic unite with incandescence. The

brittle alloy, $PtAs_2$, loses the whole of its arsenic on ignition. Platinum also forms brittle alloys with antimony, bismuth, and vanadium.

Platinum and Carbon.

637 *The Platinocyanides.*—The potassium salt is formed when a mixture of equal parts of spongy platinum and ferrocyanide of potassium is heated nearly to redness in a crucible, the mass dissolved in water, and the filtrate evaporated (Gmelin), or when platinous chloride is dissolved in cyanide of potassium.[1] The other salts can be obtained by double decomposition.

Platinocyanic Acid, $H_2Pt(CN)_4$, is obtained by decomposing the copper or mercury salt with sulphuretted hydrogen,[2] or by decomposing the barium salt with dilute sulphuric acid.[3] After evaporating to dryness, the residue is treated with a mixture of alcohol and ether, and the ethereal solution allowed to evaporate spontaneously, when fine cinnabar-red prisms, exhibiting a splendid blue colour by reflected light, are obtained. These have the composition $H_2Pt(CN)_4+5H_2O$. Sometimes yellowish-green crystals, having a copper-red or golden lustre, are obtained, which contain more water. When heated to 100° they become yellow, and decompose at temperatures above 140°. They are deliquescent, yielding a colourless solution in alcohol; the aqueous solution decomposes carbonates with evolution of carbon dioxide.

Potassium Platinocyanide, $K_2Pt(CN)_4+12H_2O$, is obtained by dissolving ammonium chloroplatinate together with caustic potash in a boiling concentrated solution of potassium cyanide. The liquid is boiled until no further evolution of ammonia takes place, when the salt crystallises out.[4] This is also formed when spongy platinum is boiled with solution of cyanide of potassium, or when a mixture of the two bodies is heated at a temperature of from 500° to 600° in steam (Deville and Debray):

$$4KCN+Pt+2H_2O=K_2Pt(CN)_4+2KOH+H_2.$$

It forms long yellow rhombic prisms, exhibiting a blue metallic lustre by reflected light, and is very readily soluble in water.

[1] Knop, *Annalen*, 1842, **43**, 111.
[2] Quadrat, *Annalen*, 1847, **63**, 164; 1848, **65**, 249; 1849, **70**, 300.
[3] Weselsky, *J. pr. Chem.* 1856, **69**, 276.
[4] Martius, *Annalen*, 1861, **117**, 357.

If the hot solution be saturated with chlorine, or boiled with aqua-regia, colourless prisms of *potassium chloroplatinocyanide*, $K_2Pt(CN)_4Cl_2+2H_2O$, are obtained on evaporation. If this solution be mixed in the right proportion with potassium platinocyanide a double salt is obtained of the composition $5K_2Pt(CN)_4+K_2Pt(CN)_4Cl_2+21H_2O$, crystallising in magnificent green prisms which exhibit a copper-red lustre by reflected light and are soluble in water. This salt, which is also formed when potassium platinocyanide is treated with a moderate quantity of chlorine, was at one time believed to be a platinicyanide corresponding to potassium ferricyanide, as the presence of chlorine in it had been overlooked, and because in alkaline solution it acts as an oxidising agent, potassium hypochlorite being formed:

$$5K_2Pt(CN)_4+K_2Pt(CN)_4Cl_2+2KOH=6K_2Pt(CN)_4+KOCl+KCl+H_2O.$$

Its true composition was first pointed out by Hadow.[1]

Barium Platinocyanide, $BaPt(CN)_4+4H_2O$, was first obtained by passing hydrocyanic acid into water containing platinous chloride and barium carbonate in suspension.[2] It can also be easily obtained by decomposing the copper salt by baryta-water. It forms large rhombic crystals which exhibit a green colour in the direction of the primary axis, whilst at right angles to this direction they appear of a sulphur-yellow colour.

Magnesium Platinocyanide, $2MgPt(CN)_4+7H_2O$, is obtained by decomposing the barium salt with magnesium sulphate, and is one of the most beautiful salts of this group. It forms large square-based red prisms, the sides of which viewed by reflected light have a beetle-green lustre, whilst the end faces reflect blue or purple light. It crystallises from alcohol with six molecules of water in four-sided lemon-yellow tables, having a blue reflection and often exhibiting all shades of colour of red, blue, and green.

Many other platinocyanides besides these are known, of which several are remarkable for their splendid play of colours. Some, such as the green copper salt, are insoluble powders obtained as precipitates by double decomposition. A very characteristic reaction for the platinocyanides is that on addition of a mercurous or a mercuric salt to their solution a

[1] *Journ. Chem. Soc.* 1861, 106.

[2] Weselsky, *J. pr. Chem.* 1856, **69**, 276.

white precipitate is first thrown down, but on addition of more mercurous salt this becomes of a smalt-blue colour.

These salts become luminous when exposed to the Röntgen rays, and are employed for making screens by means of which the absorption of these rays may be observed.

638 *Potassium Platinothiocyanate*, $K_2Pt(SCN)_4$, is obtained by dissolving platinum dichloride in a solution of potassium thiocyanate, or better by dissolving equal parts of potassium chloroplatinite and potassium thiocyanate in the smallest quantity of water, when the mixture becomes warm, and on cooling the salt separates out in red microscopic prisms. When the corresponding barium salt is decomposed by dilute sulphuric acid, the free acid is obtained in solution, but this undergoes rapid decomposition.[1]

Platinithiocyanic Acid, $H_2Pt(SCN)_6$.—On decomposing the lead salt with dilute sulphuric acid, a thick dark-red very acid liquid is obtained, which decomposes carbonates, and dissolves zinc with evolution of hydrogen. On evaporation in a vacuum an indistinct crystalline mass remains behind.

Potassium Platinithiocyanate, $K_2Pt(SCN)_6$, is obtained by adding potassium thiocyanate solution, not in excess, to a solution of potassium chloroplatinate, and heating to boiling. The filtered solution on cooling deposits large six-sided prisms or tables having a carmine-red colour and possessing a very disagreeable taste. They dissolve in water forming such a deep-red solution that one drop of the concentrated liquid imparts a distinct colour to 100,000 parts of water. When the concentrated solution is boiled with ammonium sulphate a very similar ammonium platinithiocyanate is formed. The platinithiocyanates of the alkali-metals are soluble in water and crystallisable; those of the heavy metals are insoluble and have a yellowish- or blackish-red colour (Buckton).

Detection and Estimation of Platinum.

639 If a platinum compound be heated on a carbonised match in the gas-flame a grey spongy mass is obtained soluble only in aqua-regia. The concentrated solution yields with potassium chloride and sal-ammoniac the well-known and characteristic precipitates. Sulphuretted hydrogen throws down from solu-

[1] Buckton, *Journ. Chem. Soc.* 1855, 22.

tions of a platinum salt, slowly in the cold but more quickly on heating, the brown disulphide which is soluble in an excess of yellow sulphide of ammonium. A solution of tin dichloride colours platinum chloride solutions dark-brown, inasmuch as platinous chloride is formed.

In the general separation of the metals platinum and gold are obtained together with arsenic, antimony, and tin. Their presence is indicated by the brown colour of the precipitate produced by hydrochloric acid in the solution in sulphide of ammonium. In this case the precipitate is fused with sodium carbonate and nitre, the fused mass lixiviated with water, and the residue, which may contain the gold and platinum together with tin dioxide and sodium antimonate, is treated with zinc and hydrochloric acid when the latter two compounds are reduced to metals. The mass is first boiled with hydrochloric acid to remove the tin, and next with nitric acid and a little tartaric acid to dissolve the antimony; the residue is then treated with aqua-regia, the solution concentrated and evaporated to dryness on a water-bath with an excess of sal-ammoniac, and alcohol added to dissolve the gold chloride. From the alcoholic solution the gold may be readily precipitated with ferrous sulphate. The portion insoluble in alcohol may contain ammonium chloroplatinate, and this on ignition will leave a residue of spongy platinum. The *quantitative estimation* of platinum always takes place as metal, obtained by ignition of ammonium chloroplatinate, or by heating potassium chloroplatinate in a current of hydrogen and lixiviating the residue with water, or sometimes also by ignition of the sulphide. *The atomic weight* of platinum was determined by Berzelius[1] by analysis of the potassium double chloride; the mean number obtained by him was 195·7; Andrews,[2] who employed the same method, found the atomic weight to be 196·9, but Seubert[3] obtained 193·3, and Halberstadt,[4] confirming this result, found 193·5. (O = 15·88.)

[1] *Lehrbuch*, 5*te Aufl.* **3**, 1212.
[2] *Chem. Gaz.* 1852, 379.
[3] *Annalen*, 1881, **207**, 1.
[4] *Ber.* 1884, **17**, 2963.

ARGON AND HELIUM.

ARGON = 39·64 (?)

640 In his celebrated research on the action of the electric spark on air, published in the Philosophical Transactions for 1785, Cavendish describes an experiment in which he added excess of oxygen to a given volume of air, passed electric sparks through the mixture collected over caustic potash, until no further diminution of bulk took place; he then absorbed the excess of oxygen by "liver of sulphur," "after which only a small bubble of air remained unabsorbed which certainly was not more than $\frac{1}{1\frac{1}{2}0}$th of the bulk of the phlogisticated air (nitrogen) let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{1\frac{1}{2}0}$th part of the whole."

A century elapsed before the true explanation of the existence of this small proportion of unabsorbable gas was given, viz., the presence of a constituent of the atmosphere hitherto overlooked, to which the name of Argon (*ἄργον*, idle, inactive) has been given. The volume of this gas contained in the air amounts to $\frac{1}{8\frac{1}{4}}$th part of that of the atmospheric nitrogen (or exactly 1·186 per cent.), and the history of its discovery is interesting as having been arrived at by exact physical measurements. It has already been stated (vol. i., pp. 222, 261, 450) that Lord Rayleigh determined with great care the weight of one litre of oxygen, of hydrogen, and of nitrogen. In the case of both oxygen and nitrogen Rayleigh prepared and weighed each gas by different methods. Samples of oxygen obtained by electrolysis, by heating chlorate, and by heating permanganate, proved to possess the same weight. In order to ascertain whether nitrogen was also homogeneous, Rayleigh weighed nitrogen prepared from ammonia and found that it was lighter than atmospheric nitrogen

by about one-half per cent. This amount was far above the possible experimental error and pointed to a distinct difference between the gas obtained from the two sources. What that difference might be was at first not clear, and many possible explanations were put forward. In 1894, Professor W. Ramsay associated himself with Lord Rayleigh, and they proved that the above difference was due to the presence in the atmosphere of an inert gas heavier than nitrogen.[1] In order to collect argon from the air three methods are available: (1) to pass atmospheric nitrogen over red hot turnings of magnesium; (2) to "spark" the gas with excess of oxygen in presence of caustic alkali; (3) to dissolve the more soluble argon in water. The apparatus used for the first of these is shown in Fig. 187. Atmospheric nitrogen is passed from gas-holder (A) to gas-holder (B) through a tube (G) filled with magnesium heated to redness to absorb nitrogen; over red hot copper oxide (*a*)(*b*) so as to ensure that any carbonaceous matter shall be burnt to carbon dioxide and water, these being absorbed by soda-lime placed in (F) and (I); (D) and (H) are drying tubes filled with phosphorus pentoxide. After passing the gas backwards and forwards for about seven days the volume of the original nitrogen was reduced to $\frac{1}{80}$th, and the density of the gas was 16·1, whilst a second

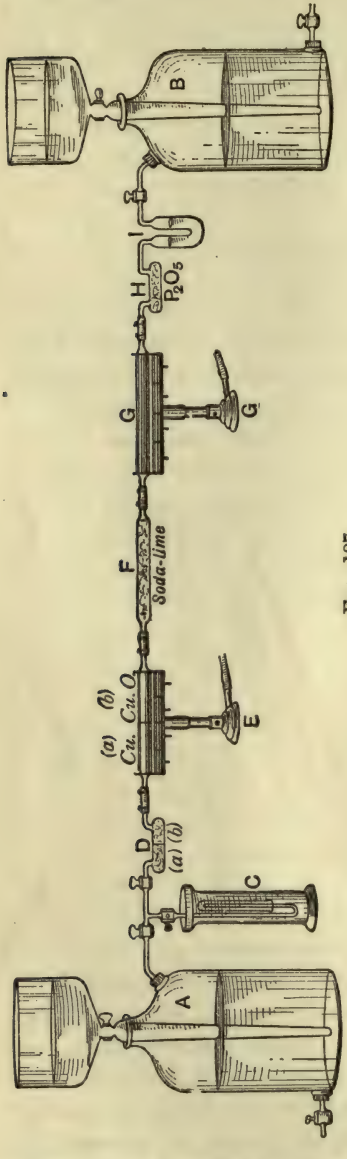


Fig. 187.

[1] *Phil. Trans.* 1895, 187.

treatment with fresh magnesium further reduced the volume and increased the density to 19·94. The second method is an improvement on Cavendish's original experiment by which the nitrogen is oxidised and absorbed by alkali as a mixture of nitrite and nitrate. The apparatus employed is shown in Fig. 188. Atmospheric nitrogen is passed from one gas-holder to another (not shown in the Fig.) through a large glass balloon containing two copper electrodes with thick platinum terminals and tubes for supplying a constant stream of caustic soda solution. This latter serves to keep the surface of the globe cool and to absorb the nitrous fumes formed by the action of the electric arc obtained by a powerful alternating current on the mixture of oxygen and nitrogen.

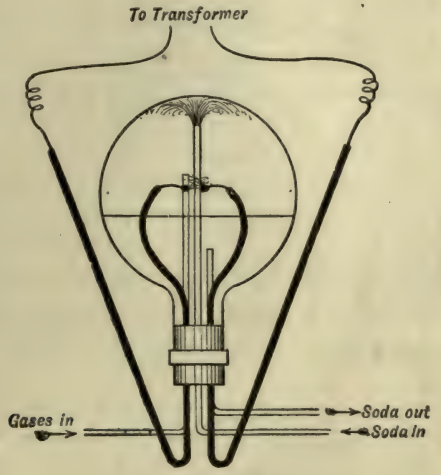


FIG. 188.

The third method is based upon the fact that argon is considerably more soluble in water than nitrogen; at the ordinary atmospheric temperature 100 volumes of water absorb about 1·5 volumes of nitrogen and 4·5 volumes of oxygen from air, whereas four volumes of argon are dissolved. On boiling the water a mixture of oxygen and argon with traces of nitrogen is obtained. The separation of oxygen and argon is a comparatively simple matter, as it is only necessary to pass the mixture over red hot copper. From the foregoing it would appear likely that argon would be contained dissolved in mineral and other waters, and this has been found to be

the case. Many of these contain notable quantities of argon, but experiment has hitherto failed to detect this substance in the bodies of either plants or animals. Argon has also been found together with helium in the gas evolved on heating numerous minerals, and also from one specimen of meteoric iron. (See Helium.)

Properties.—One litre of argon weighs 1·7818 gram, and its density is 19·82 (H = 1). Hence a mixture of 98·814 volumes of nitrogen and 1·186 volumes of argon weighs 1·2574 gram. The actual experimental weight obtained by Rayleigh was 1·2572 gram. All attempts to combine argon with other elements have hitherto failed. As has been stated it does not combine with oxygen under the influence of the electric discharge, nor with metallic magnesium. No action is observed when argon is sparked with chlorine or with hydrogen. It is not absorbed or altered in volume when passed through a red hot tube together with the vapours of phosphorus, sulphur, tellurium or sodium. Fused alkalis and alkali peroxides do not act upon it, nor does nascent chlorine. Fluorine, the most active of the elements, does not enter into combination with argon, and this gas suffers no diminution in volume when sparked with the vapour of carbon tetrachloride nor when passed over heated titanium and uranium. Argon has been condensed to a colourless liquid, which boils under atmospheric pressure at −187° and freezes to an ice-like solid at −189·6°. The critical point is −121°.[1]

Spectrum of Argon.—The spectrum of argon is extremely characteristic, and has been carefully examined.[2] Two different spectra are obtained according to the tension of the gas and the strength of the electric discharge; with a tension of 3 mm. an orange glow is observed in the tube, and the spectrum (Fig. 189) shows a large number of lines in the red, two of which, having wave lengths of 6965·6 and 7056·4, are especially prominent. Bright lines are also observed in all parts of the spectrum, the most noticeable being the line 6038·4 in the yellow, five lines in the green, the two brightest having wave lengths of 5610 and 4702 respectively, and five in the violet, the brightest of which has a wave length of 4200. With a lower tension of the gas and a stronger electric discharge, the

[1] Olszewski, *Phil. Trans.* 1895, 253.

[2] Crookes, *Phil. Trans.* 1895, 243; Kayser, *Chem. News*, 1895, **72**, 99; Eder and Valenta, *Monatsh.* 1895, **16**, 893; 1896, **17**, 50.

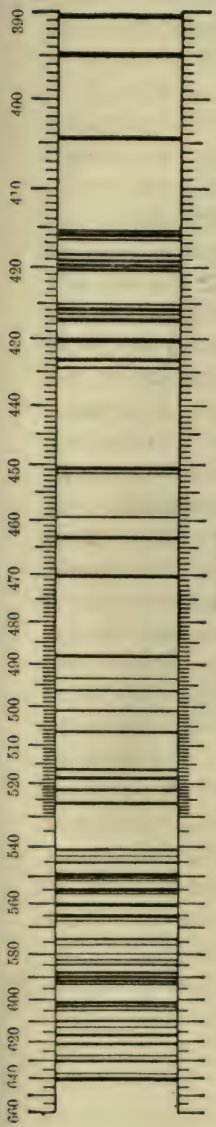


FIG. 189.

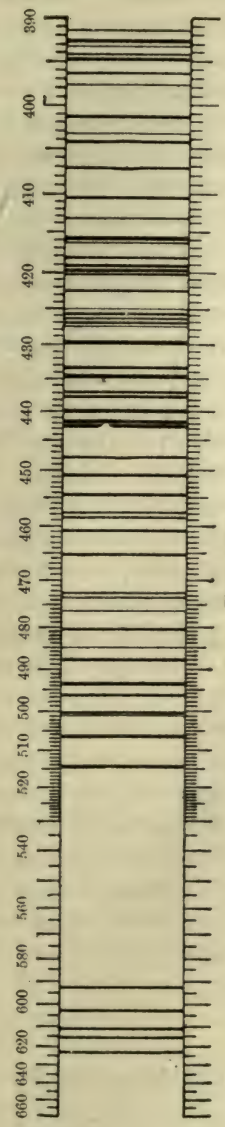


FIG. 190.

FIG. 191.

tube shows a bluish glow, and the spectrum consists of 119 lines (Fig. 190).

Atomic Weight of Argon.—From the foregoing it is evident that all attempts to determine the atomic weight of argon must be based upon physical rather than on chemical methods. The method of ascertaining the atomic weight by means of the determination of the specific heat of the element (see p. 15) was not applicable to the case of argon, as for this purpose a practically unlimited supply of a gaseous element is needed. By employing another method, however, conclusions can be arrived at. The ratio between the two specific heats of the gas—that at constant temperature and that at constant pressure—may be calculated from the velocity of sound in that gas (p. 27). This latter can be ascertained, relatively to air, by Kundt's method of observing the nodes of compression in air and then in argon enclosed in a glass tube containing lycopodium, the tube being rubbed so as to produce a shrill tone. Experiment showed that the above ratio in the case of argon is 1 to 1·66, closely corresponding with that found by Kundt for gaseous mercury, viz. 1 to 1·67 (see p. 27), but different essentially from the ratio obtained for oxygen, hydrogen, nitrogen, carbon monoxide and other gases containing two atoms in the molecule, namely 1 to 1·4. This evidence goes to show that argon molecules like those of mercury (p. 28) are monatomic, and that its atomic weight is 39·64 (O = 15·88). This number would place argon between potassium and calcium in Mendeléeff's table (see p. 45), but there is no vacant space between these two elements. Hence it has been suggested that the so-called argon is a mixture of two or more elements of different densities. Against this view are to be placed the facts (1) that argon has a definite boiling- and melting-point, (2) that on diffusing argon through a porous diaphragm many times, no difference in density could be observed between the portion of gas diffused and that remaining undiffused (see vol. i., p. 63).

HELIUM = 3·96 (?)

641 In the year 1868, Lockyer observed in the spectrum of the solar chromosphere a line in the yellow nearly coincident with the double line of sodium, which he denoted as D_3, the

wave length of which is 5,875. No terrestrial substance was known containing a corresponding line in its spectrum, and Lockyer and Frankland supposed that this line was due to the presence in the sun of an element which had not been discovered in terrestrial matter, and they therefore proposed for it the name helium (ἥλιος, the sun). In 1889, Hillebrand[1] examined the action of dilute sulphuric acid on the mineral uraninite, which consists essentially of a uranate of uranyl and lead containing rare earths, and obtained a gas which he found to have the usual properties of nitrogen, and proved that this gas was actually present. After the discovery of argon, Ramsay examined the gas from the mineral cleveite, which is a variety of uraninite, thinking that this might contain argon. The result of his investigation showed that the gas from this mineral contained very little if any nitrogen; the spectrum showed that a small quantity of argon was present, but in addition other bright lines were noticed which did not occur in the argon spectrum. The most prominent of these was a line in the yellow, which appeared to correspond with the line D_3 in the chromospheric spectrum, and this conclusion was confirmed by the exact measurements of Crookes.

Further investigation then showed that helium may also be obtained by heating a considerable number of minerals, although in most cases the quantity obtained is small. Most of the minerals which yield the gas contain uranium, and the few in which uranium is not present contain yttrium or thorium. The three minerals which yield helium in the largest quantity are cleveite, the analogous bröggerite, and the uraninite first examined by Hillebrand. The gas obtained from the latter contains at least 10 per cent. of nitrogen, which accounts for the results obtained in his original investigation. Helium has also been found, together in one case with argon, in the gases evolved from certain specimens of meteoric iron, whilst others give neither of these elements, and it has also been found in the gases from the mineral springs of Cauterets in the Pyrenees and of Wildbad.

In order to prepare helium, one of the above minerals is powdered and heated in an evacuated tube, the gas evolved being collected over mercury. Any admixed gases, such as hydrogen, oxygen, carbonic dioxide, hydrocarbons, &c., may be removed in the usual manner, and nitrogen by passing frequently over

[1] *Bull. U.S. Geol. Survey*, **78**, 43.

strongly heated magnesium. Argon cannot be removed by chemical means, but may be separated by diffusion (see below).[1]

Properties of Helium.—Like argon, helium is remarkable for its inert behaviour, all attempts to cause it to enter into chemical combination having hitherto been without success. Our knowledge is at present, therefore, confined to its physical properties.

The spectrum of helium is very characteristic; in addition to the yellow line D_3, (which, with instruments giving a wide dispersion, is found to be a double line), four other bright lines occur in the red, the blue-green, the blue and the violet, and many other fainter lines have been mapped not only in the visible but also in the ultra-violet and infra-red portions. Fig. 191 gives the spectrum of impure helium as observed by Runge, in which the lines due to helium are marked with an asterisk. In discussing the relations between the lines of a spectrum (p. 136) it has already been mentioned that from the examination of these relations in the helium spectrum, Runge and Paschen concluded that the gas prepared as above must contain two elements, and diffusion experiments showed that the gas could be divided into a lighter and heavier portion having somewhat different spectra. The further work of Ramsay has shown that the gas obtained from the above minerals, which has a mean density of 2·165 (O = 15·88), when subjected to systematic diffusion, may be separated into a portion having a density of 1·98 (H = 1), and another of density 2·27. The former undergoes no change when subjected to further diffusion, but still shows the same spectrum as the original gas; whilst the heavier fraction on further diffusion gives a still heavier residue, the spectroscopic observation of which shows the presence of argon, which is evolved in small quantities from the minerals. The differences in the spectra observed by Runge and Paschen may be brought about by alteration in the pressure of the gas in the vacuum tube. These results therefore afford no confirmation of Runge and Paschen's supposition.[2]

The density of helium, as already mentioned, is 1·98 and the determination of the velocity of sound in the gas has shown that the ratio of the specific heats (p. 27) is 1·65, and it would therefore appear that, as in the case of mercury and argon, the

[1] Ramsay, *Proc. Roy. Soc.* May 2nd, 1895; Ramsay, Collie, and Travers, *Journ. Chem. Soc.* 1895, i. 684; *Nature*, 1897, **56**, 378.

[2] *Nature*, 1897, **53**, 380, 461.

molecules of this gas are monatomic; the atomic weight of helium is therefore 3·96 (O = 15·88).

Helium is the least soluble in water of all known gases, 100 c.c. of water dissolving only 0·7 c.c. of the gas. It has also hitherto resisted all attempts to liquefy it,[1] having apparently a lower boiling point than hydrogen.

The existence of two substances having the properties of argon and helium is not any way indicated in the periodic classification of the elements (p. 62), and it is probable that their discovery will lead to modifications of that hypothesis, but too little is yet known of these substances to allow of any definite theoretical conclusions being arrived at.

[1] *Nature*, 1896, **54**, 377.

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